# PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL USING ULTRASONIC TUBULAR REACTOR

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This thesis is dedicated to

my wife Yuliani,

my daughter Arini Khansa Khaifah,

my family,

and my friends.

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# ABSTRACT

The aim of study is to produce the synthesis of biodiesel from waste cooking oil (WCO) using ultrasonic tubular reactor at laboratory scale. The experiment was used to determine the effect of ester contents by reaction time, molar ratio of WCO to Methanol (MeOH), amount of catalyst, frequency of ultrasonic and ultrasonic output power using ultrasonic tubular reactor. Based on the optimum process by ultrasonic tubular reactor, a comparisons study of three different processes (ultrasonic tubular reactor, conventional ultrasonic cleaner and mechanical stirring) were also investigated. The optimum results of biodiesel process using ultrasonic tubular reactor are the reaction time of 5 minute, sodium hydroxide (NaOH) catalyst 1%wt of WCO, molar ratio WCO to MeOH of 1:6, frequency ultrasonic of 20 KHz and ultrasonic output power of 650 Watt. The reaction time was reduced to 12-24 times (minute) compare to mechanical stirring and the ester contents was obtained at 96.54%wt. The ternary phase diagram ultrasonic tubular reactor was to find out the liquid liquid-equilibrium base on WCO- Fatty Acid Methyl Esters (FAME) -MeOH. The results show that by increasing the residence time of the whole reactant system within the two-phase zone is good for the reaction transesterification on ultrasonic tubular reactor. The semi continuous ultrasonic tubular reactor for biodiesel process of WCO gave conversion of WCO to FAME of 98%wt with flow rate of 5.56 ml/s. Meanwhile, the pilot plan of biodiesel facilities using mechanical stirring method (capacity of 100 kg WCO/batch) was designed and the transfer knowledge about biodiesel process was a success between the university with industry in Batu Pahat.

# ABSTRAK

Tujuan kajian yang telah dijalankan adalah untuk menghasilkan sintesis biodiesel daripada minyak masak terpakai dengan menggunakan reaktor ultrasonik tubular didalam skala makmal. Rekabentuk eksperimen yang digunakan untuk mendapatkan kandungan ester dipengaruhi oleh masa tindakbalas, kadar kemolaran minyak masak terpakai kepada Metanol, jumlah pemangkin, frekuensi ultrasonik, dan output kuasa ultrasonik menggunakan reaktor ultrasonik tubular. Berdasarkan kepada proses reaktor ultrasonik tubular yang optimum, perbandingan antara tiga proses yang berbeza (reaktor ultrasonic tubular, permbersih ultrasonik konvensional dan pengadukan secara mekanikal) juga dikaji. Hasil optimum daripada proses biodiesel menggunakan reaktor ultrasonik tubular ialah masa tindakbalas lima (5) minit, 1%wt pemangkin NaOH bagi minyak masak terpakai, Nisbah kemolaran minyak masak terpakai kepada MeOH ialah 1:6, 20 KHz frekuensi ultrasonik dan 650 Watt output kuasa ultrasonik. Masa tindakbalas dikurangkan kepada 12-24 kali (minit) dibandingkan kepada dua (2) lagi kaedah dan kandungan ester yang diperolehi ialah 96.54 %wt. Rajah fasa ternary reaktor ultrasonik tubular adalah untuk mendapatkan keseimbangan cecair diantara minyak masak terpakai- asid lemak metil ester-MeOH. Keputusan menunjukkan peningkatan masa penghapusan bagi keseluruhan sistem tindakbalas dalam zon dua fasa adalah baik bagi tindakbalas pengtransesteran pada reaktor ultrasonik tubular. Reaktor ultrasonik tubular semi-berterusan bagi proses biodiesel daripada minyak masak terpakai memberi penukaran minyak masak terpakai kepada asid lemak metil ester sebanyak 98%wt dengan kadar alir sebanyak 5.56 ml/s. Sementara itu, loji pandu bagi kemudahan biodiesel menggunakan kaedah pengadukan secara mekanikal (kapasiti sebanyak 100 kg minyak masak terpakai/kelompok) telah direka dan pemindahan pengetahuan tentang proses biodiesel dilakukan antara universiti dengan industri di Batu Pahat telah berjaya.

# CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

## LIST OF SYMBOLS AND ABBREVIATIONS

| | |
|---|---|
| $Al_2O_3$ | - Aluminum Oxide |
| ASTM | - American Society For Testing And Materials |
| ATR-IR | - Attenuated Total Reflection Infrared Spectroscopy |
| $-C–CH_2–O^-$ | - Alkoxide Ion |
| $-CH_3$ | - Methyl Group |
| $CO_2$ | - Carbon Dioxide |
| CWCO | - Crude Waste Cooking Oil |
| DEE | - Diethyl Ether |
| DG | - Diglyceride |
| DME | - Dimethyl Ether |
| EN | - European Normalization |
| FAEE | - Fatty Acid Ethyl Ester |
| FAME | - Fatty Acid Methyl Ester |
| FFA | - Free Fatty Acid |
| FID | - Flame Ionization Detector |
| GC | - Gas Chromatography |
| $K_2CO_3$ | - Potassium Carbonate |
| KOH | - Potassium Hydroxide |
| LLE | - Liquid – Liquid Equilibrium |
| MeOH | - Methanol |
| MG | - Monoglyceride |
| MSTFA | - N-Methyl-N-Trimethylsilyl Trifluoroacetamide |
| NaOH | - Sodium Hydroxide |
| Naγ | - Gamma Sodium |
| $O-CH_3$ | - Methoxide Group |
| OFR | - Oscillatory Flow Reactor |

| | | |
|---|---|---|
| SCFs | | - Supercritical Fluid Continues |
| SFC | | - Supercritical Fluid |
| TBME | | - Tert-Butyl Methyl Ether |
| TG | | - Triglyceride |
| THF | | - Tetrahydrofuran |
| UTHM | | - Universiti Tun Hussein Onn Malaysia |
| WCO | | - Waste Cooking Oil |
| *AV* | - | Acid Value |
| *C* | - | Ester Contents |
| *GT* | - | The Percentage (m/m) of Total Glycerol (Free And Bound) In The Sample |
| *ml* | - | millimeter |
| $\rho$ | - | Density |

# LIST OF APPENDICES

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of study

Biodiesel is an alternative diesel fuel derived from vegetable oils or animal fats (Ma & Hanna, 1999) or mono-alkyl esters of long chain fatty acids derived from a renewable lipid feedstock. The main advantages of using biodiesel fuel are renewable, better quality of exhaust gas emissions, biodegradability and, given that all the organic carbon present is photosynthetic in origin, it does not contribute to a net rise in the level of carbon dioxide in the atmosphere if all of the energy inputs for the biodiesel production are non-fossil-based, and consequently to the greenhouse effect (Barnwal & Sharma, 2005).

In the South East Asia, Malaysia is one of the countries which actively produce oil for the commercial production and usage biodiesel as fossil fuels replacement due to its rich palm oil resources. The current approved installed capacity for biodiesel production is about 10.2 million tons in Malaysia (Puah & Choo, 2008). Malaysia is now looked upon as the pioneer palm biofuel producer. Malaysia has embarked on a comprehensive palm biofuel programmed since 1982 and has successfully established the use of palm methyl esters and the blend of processed palm oil (5%) with petroleum diesel (95%) as a suitable fuel for the transport and industrial sectors. Currently, the major concern for biodiesel production is economic feasibility. Biodiesel production will not be favored without tax exemption and subsidy from government; as the production cost is higher than fossil derived diesel (Demirbas & Balat, 2006). The overall biodiesel cost consists of raw material (production and processing), catalyst, biodiesel processing (energy,

consumables and labor), transportation (raw materials and final products) and local and national taxes (Haas *et al*., 2006). Most biodiesel plants are using refined vegetable oils as their main feedstock. Therefore, the cost of refined vegetable oils contributed nearly 80% of the overall biodiesel production cost (Lam *et al*., 2009). Thus, it is undeniable that feedstock will be the most crucial variable affecting the price of biodiesel in the global market.

In order to overcome this limitation, biodiesel manufacturer are focusing their attention on using low-cost feedstock such as waste cooking oil in order to ensure economic viability in biodiesel production. Waste cooking oil (WCO) is far less expensive than refined vegetable oils and therefore has become a promising alternative feedstock to produce biodiesel. In fact, generation of waste cooking oil in any country in the world is huge, and may result to environmental contamination if no proper disposal method is implemented. Table 1.1 showed that, the estimation of waste cooking oil produced in selected countries (Gui, Lee & Bathia, 2008). Based on the table, waste cooking oil generated is more than 15 million tones. However, it is estimated that the WCO collected in Malaysia, is 0.5 million per year. This collected material is a good commercial choice to produce biodiesel due to its low cost. It should be noted that the actual amount of waste oil produced is much higher based on global production.

Table 1.1: Quality of waste cooking oil produces in selected countries. (Gui *et al*, 2008)

| Country | Quantity (million tones/year) |
|---|---|
| China | 4.5 |
| European | 0.7 – 1.0 |
| United States | 10.0 |
| Japan | 0.45 – 0.57 |
| Malaysia | 0.5 |
| Canada | 0.12 |
| Taiwan | 0.07 |

With the increase in the demand for biodiesel, new methods of increasing and enhancing biodiesel production are being researched. The commercial method of biodiesel production is time consuming and energy intensive. It is a conventional process that requires maintaining the reactants at a temperature of 60 °C for 1–2 h and yield of 97–98% (Chand, 2008). Al-Widyan & Al-Shouykh, (2002) reported the

transesterification process of waste palm oil to biodiesel with 2.25 M sulfuric acid as catalyst, 3 hours of time reaction and ester yields of 90%. Dias *et al*, (2008), established of biodiesel process using mechanical stirring gives yields of ester up to 97% in 60 minutes, molar ratio of 1:6 (oil to methanol) at 70$^{o}$C. Veljkovic *et al*, (2006), reported the production of biodiesel from tobacco seed oil using two step reactions with optimum condition in 30 minute at 60$^{o}$C of reaction temperature and yield of FAME about 91%.

## 1.2 Problem statement

The mechanical stirring method in transesterification reaction can only occur in the interfacial region between the liquids and also WCO and alcohols are not totally miscible, this is a very slow process. A vigorous mixing is required to increase the area of contact between the two immiscible phases, and thus produce an emulsion.

Ultrasonic is one of the alternative methods to high mixing. However, conventional ultrasonic systems are based on the relatively-fixed resonant frequency of the transducers used, small capacity and inefficient sonochemistry reactors. Therefore, an ultrasonic tubular reactor is one of modification tools for reaction of biodiesel. It is designed with piezoelectric transducers type at the tube to provide the longitudinal vibration. The tube is driven by the transducers and can effectively transform the longitudinal vibration into the radial vibration; moreover, the frequency and the output power can be adjustable. The key benefit to this tubular reactor system is the possibility to make batch or inline flow through production.

## 1.3 Objectives of study

The objective of this study was:

(a) To study the experimental variables for the production of biodiesel conversion using ultrasonic tubular reactor

(b) To design suitable plant for small-scale production of biodiesel process from waste cooking oil.

## 1.4 Scopes of study

In achieving the objective of the research, important tasks need to be carried out comprising of four research scopes such as:

(a) Comparison method of mechanical stirring and type of ultrasonic (ultrasonic tubular reactor and ultrasonic cleaner) in conversion of waste cooking oil to biodiesel. On other hand, to find the effect of reaction time and molar ratio oil to methanol in ultrasonic tubular reactor was conducted. The calculation of conversion WCO to biodiesel by means of acid value analysis.
(b) Transesterification of waste cooking oil was conducted using ultrasonic tubular reactor with close system at different reaction time, amount of catalyst, molar ratio oil to methanol, ultrasonic output power, and frequency.
(c) Liquid-liquid equilibrium (LLE) of three phases between FAME, methanol and WCO in different molar ratio oil to methanol, amount of catalyst and frequency of ultrasonic was investigated. Reaction time is base on variation in ternary diagram.
(d) The results of biodiesel were subjected to comprehensive the chemical and physical tests using attenuated total reflection **i**nfrared spectroscopy (ATR-IR), gas chromatography (GC), acid value by titration, density at $40^{o}$C, kinematic viscosity at $40^{o}$C, water contents and flash point.

## 1.4 Significant of study

Biodiesel is a liquid transportation fuel that can be produced from renewable raw material such as waste cooking oil. The use of cooking oil as raw material for biodiesel production will enhance the viability of the food industry in Batu Pahat.

Technologies of transesterification of vegetable oils into Fatty Acid Methyl Esters (FAME) called Biodiesel, have been experimentally established and are well documented in the open literature. But, no previous work using ultrasonic tubular reactor in biodiesel process was explored. This study will provide useful data for society in the biodiesel process.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

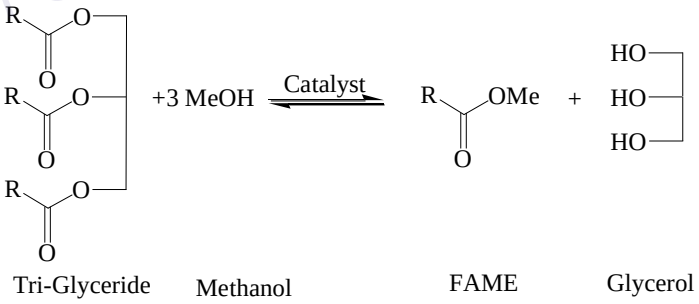
For the last century, petroleum derived fuels have been the major source of the world's energy. However, it is predicted that fossil oil will be depleted in the near future. In addition to that, environmental concerns have trigged the examination of alternative energy sources. Future projections indicate that economics and energy needs will increase the focus on the production of synthetic fuels derived from non-petroleum sources, including biomass and waste products among others (Ghassan, Al-Widyan & Al-Shyouck, 2002).

The higher public awareness in recent years of the impacts of fossil fuel emissions on the environment and their potential health hazards triggered the government to impose restrictions on fossil combustion emissions. One way to solve the problem mentioned above is to look for alternative and renewable energy sources. One of the most promising alternative energy sources is biomass (Peterson *et al.,* 1995). It is renewable, available everywhere and contains much less sulfur and nitrogen, which makes it more environmentally friendly than fossil sources. Among the biomass sources, waste vegetable oils and animal fats have attracted much attention as a potential renewable resource for production of an alternative for petroleum based diesel fuel. Most of the investigations reported in the literature on the usage of vegetable oil as engine fuels have emphasized modifying the oil to work in existing engine designs. The primary problem associated with using straight vegetable oils as a fuel in a compression ignition engine is the high viscosity (Yahya & Marley, 1994). Among the methods that have been investigated was transforming

the vegetable oils to their corresponding esters. The fuel characteristics of these esters are much closer to those of diesel fuel than those of the fresh vegetable oils (Clark *et al.*, 1984). In the 1970s, it was found that the viscosity of vegetable oils could be decreased through a simple chemical process. The process yields a vegetable oil based fuel that works as efficiently as diesel fuel in modern diesel engines. This fuel is called biodiesel, and the process is called transesterification. It is a chemical process in which a triglyceride in the vegetable oils and fat reacts with alcohol in the presence of a strong acid or base to produce a mixture of fatty acids alkyl esters (FAME) and glycerol.

## 2.2 Biodiesel

Biodiesel is an alternative diesel fuel derived from vegetable oils or animal fats. The main components of vegetable oils and animal fats are triglycerides or also known as esters of fatty acids attached to a glycerol. Normally, triglycerides of vegetable oils and animals fats consist of several different fatty acids. Different fatty acids have different physical and chemical properties and the composition of these fatty acids will be the most important parameters influencing the corresponding properties of a vegetable oils and animal fats. The reaction of biodiesel was shown in the Figure 2.1.




where R denotes a hydrocarbon chain of carbon number 12~18.

Figure 2.1: Chemical reaction of biodiesel (Freedman *et al.*, 1986).

The reaction associated with biodiesel production is a transesterification reaction. This is a reaction that converts one form of ester to another. Vegetable oils are triglyceride esters (esters of 3 molecules of fatty acids with one molecule of

glycerol). They react with monohydroxy alcohols like methanol and ethanol, producing corresponding esters. Glycerol is the by-product.

### 2.2.1 Composition of biodiesel

Making Biodiesel is defined chemically as a reaction between an alcohol and a long chain fatty acid. In the case when methanol is used as reactant, it will be a mixture of fatty acid methyl esters (FAME) whereas if ethanol is used as reactant, the mixture will be fatty acid ethyl esters (FAEE). However, methanol is commonly and widely used in biodiesel production due to their low cost and availability. Ethanol or Ethyl Alcohol can also be used but with problems. It needs to be as pure (water free) as possible. Ethanol containing as little as 2% water will not make biodiesel. If you have dry ethyl alcohol, and make good biodiesel, the glycerin may not separate from the biodiesel without help (Alok, 2008).

Based on different feedstock, the biodiesel produced will have different composition of FAME. Table 2.1 is shown the common composition of FAME in biodiesel (Alok, 2008).

Table 2.1: Chemical structures of common FAME. (Alok, 2008)

| No | Components | Chemical Formula | Molecular weight (kg/mol) |
|---|---|---|---|
| 1 | Methyl Myristate | $C_{14}H_{30}O_2$ | 242.41 |
| 2 | Methyl Pentadecanoate | $C_{16}H_{32}O_2$ | 256.42 |
| 3 | Methyl Palmitate | $C_{17}H_{34}O_2$ | 270.457 |
| 4 | Methyl Stearate | $C_{19}H_{38}O_2$ | 298.511 |
| 5 | Methyl Oleate | $C_{19}H_{36}O_2$ | 296.495 |
| 6 | Methyl Linoleate | $C_{19}H_{34}O_2$ | 294.479 |
| 7 | Methyl Linolenate | $C_{19}H_{24}O_2$ | 292.463 |

### 2.2.2 Benefits of biodiesel

One of the main driving forces for biodiesel widespread use is the limitation of greenhouse gas emissions ($CO_2$ being the major one) by the Kyoto Protocol. Along

with ethanol and other biomass derived fuels, biodiesel is an important bio-energy. When plants photosynthesize, they use the sun's energy to pull $CO_2$ out of the atmosphere and incorporate it into biomass. Part of the solar energy is locked into the chemical structure within the biomass. There are a number of thermal, chemical or microbial processes that can be used to release this energy or convert it into a more convenient form for human use. As a form of bio-energy, biodiesel is nearly carbon-neutral, i.e., the $CO_2$ it produces on burning will be absorbed naturally from $CO_2$ in the air and recycled without an overall net increase in the atmospheric $CO_2$ inventory, thus making an almost zero contribution to global warming (Van Gerpen *et al*., 2004).

There are many distinct benefits of using biodiesel compare to diesel fuel (Cao, 2008):

(a) Considered to be environmental friendly, biodiesel is one of the most renewable fuels compare to diesel fuel.

(b) It is biodegradable.

(c) It is derived from a renewable domestic resource, thus reducing dependence on and preserving petroleum. It can be domestically produced, offering the possibility of reducing petroleum imports,

(d) Reductions of most exhaust emissions relative to conventional diesel fuel, generating lower emissions of hydrocarbons, particulates and carbon monoxide;

(e) Biodiesel has a relatively higher flash point, >150 °C, indicating that it presents a very low fire hazard; leading to safer handling and storage,

(f) Biodiesel provides greater lubricity than petroleum diesel, thus reducing engine wear. In fact, biodiesel can be used as a lubricity enhancer for low-sulphur petroleum diesel formulations,

(g) Toxicity tests show that biodiesel is considerably less toxic than diesel fuel (Haws, 1997).

(h) Biodiesel can be used directly in most diesel engines without requiring extensive engine modifications.

## 2.3. Composition of vegetable oil

Vegetable oils and animal fats usually have hydrophobic properties, which mean they are insoluble in water. As mention earlier, triglycerides are made up of 1 mol glycerol and 3 mol fatty acids. Fatty acids vary in terms of carbon chain length and number of unsaturated bonds (double bonds). Typical fatty acids compositions found in several vegetable oils are summarized in Table 2.2 (Alok, 2008). Fatty acids that have no double bonds are termed "saturated" such as stearic acid. These chains contain maximum number of possible hydrogen atoms per atom carbon. Fatty acids that have double bonds are termed "unsaturated" such as linoleic acid. These chains do not contain maximum number of hydrogen atoms due to the presence of double bond(s) on some carbon atoms.

Normally, natural vegetable oils and animal fats are obtained in the crude form through solvent extracting or mechanically pressing, containing a lot of impurities such as free fatty acids, sterols and water. In fact, these free fatty acids and water content will have significant effect on the transesterification reaction, especially if a base catalyst is used. They could also interfere with the separation of FAME and glycerol during water washing (purification step) because of soap formation.

Table 2.2: Typical fatty acid composition (%) for different common oil source. (Alok, 2008)

| Fatty Acid composition (%) | Soybean oil | Cottonseed oil | Palm oil | Lard oil | Tallow oil | Coconut oil |
|---|---|---|---|---|---|---|
| Lauric (C12:0) | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 46.5 |
| Myristic (C14:0) | 0.1 | 0.7 | 1.0 | 1.4 | 0.8 | 19.2 |
| Palmitic (C16:0) | 0.2 | 20.1 | 42.8 | 23.6 | 23.3 | 9.8 |
| Stearic (C18:1) | 3.7 | 2.6 | 4.5 | 14.2 | 19.4 | 3.0 |
| Oleic (C18:2) | 22.8 | 19.2 | 40.5 | 44.2 | 42.4 | 6.9 |
| Linoleic (C18:2) | 53.7 | 55.2 | 10.1 | 10.7 | 10.7 | 2.2 |
| Linolenic (C18:3) | 8.6 | 0.6 | 0.2 | 0.4 | 0.4 | 0.0 |

## 2.4 Waste cooking oil as feedstock of biodiesel

The term "waste cooking oil" (WCO) refers to vegetable oil which has been used in food production and which is no longer viable for its intended use. WCO arises from many different sources, including domestic, commercial and industrial. WCO is a potentially problematic waste stream which requires to be properly managed. The disposal of WCO can be problematic when disposed, incorrectly, down kitchen sinks, where it can quickly cause blockages of sewer pipes when the oil solidifies. Properties of degraded used frying oil after it gets into sewage system are condusive to corrosion of metal and concrete elements. It also affects installations in waste water treatment plants. Thus, it adds to the cost of treating effluent or pollutes waterways (Szmigielski, Maniak & Piekarski, 2008).

Any fatty acid source may be used to prepare biodiesel. Thus, any animal or plant lipid should be a ready substrate for the production of biodiesel. The use of edible vegetable oils and animal fats for biodiesel production has recently been of great concern because they compete with food materials - the food versus fuel dispute (Pimentel *et al.*, 2009; Srinivasan, 2009). There are concerns that biodiesel feedstock may compete with food supply in the long-term (Lam *et al.*, 2009; Metzger, 2009). .

From an economic point of view; the production of biodiesel is very feedstock sensitive. Many previous reports estimated the cost of biodiesel production based on assumptions, made by their authors, regarding production volume, feedstock and chemical technology (Canakci & Van Gerpen, 2003; Zhang *et al.*, 2003; Kulkarni & Dalai, 2006). In all these reports, feedstock cost comprises a very substantial portion of overall biodiesel cost.

Haas *et al.*, (2006) developed a computer model to estimate the capital and operating costs of a moderately-sized industrial biodiesel production facility. Calculated production costs included the cost of the feedstock and of its conversion to biodiesel. The model is flexible in that it can be modified to calculate the effects on capital and production costs of changes in feedstock cost, changes in the type of feedstock employed, changes in the value of the glycerol co-product and changes in process chemistry and technology. The authors reported that for biodiesel produced from soybean oil, the cost of the oil feedstock accounted for 88 % of total estimated production costs (Haas *et al.*, 2006).

Marchetti, Miguel & Errazu, (2008) used a conceptual design of alternative production plants with a techno-economic analysis in order to compare these alternatives. In all cases, more than 80 % of the production cost is associated with the feedstock itself and consequently, efforts should be focused on developing technologies capable of using lower-cost feedstock, such as recycled cooking oils. Reusing of these waste greases not only reduce the burden of the government in disposing the waste, maintaining public sewers and treating the oily wastewater, but also lower the production cost of biodiesel significantly. (Refaat, 2010)

## 2.5 Current of biodiesel technologies

Several alternatives are been employed to increase the conversion rates and the yields of esters in order to lower production costs and improve biodiesel product quality and presented as follows;

### 2.5.1 Catalytic conversion

The problems associated with the homogeneous catalysts are the high consumption of energy and expensive separation of the homogeneous catalyst from the reaction mixture. Alternative heterogeneous catalysts have been successfully explored (Ma & Hanna, 1999) to circumvent the difficulties with homogeneous catalysts for transesterification of high FFA-containing oils.

Heterogeneous catalyst developed to eliminate the need for aqueous quenching and elimination metal salts (soaps) (Zhou & Boocock, 2006) but the conversion for most of the heterogeneous are not high enough to be used for industrial based production (Xie, Pen & Chen, 2006) and relatively prolonged reaction period. There have also been experiments aimed at replacing the sodium and potassium compounds with basic ammonium compounds as catalysts or reactants such as amines, amino guanidines, nitro guanidine's and triamino (imino) phosphoranes. The guanidines are the more active catalysts, the activity following their relative basicity. At a concentration of 3% was similar to that of potassium carbonate at the same concentration. The saturated aqueous solution of guanidine

carbonate has a pH of 11 to 11.5. The aqueous solution of free guanidine, on the other hand, gives just as strong an alkaline reaction (Schuchardt *et al*., 1998). KOH loaded on $Al_2O_3$ and Naγ zeolite supported as heterogeneous catalysts, though leaching of potassium species in both spent catalysts was observed, biodiesel yield of 91.07% was reported (Noiroj *et al.,* 2009) at temperatures below 70$^{o}$C within 2–3 h at a 1:15 molar ratio of palm oil to MeOH and a catalyst amount of 3–6 wt%.

### 2.5.2 Supercritical process

Trigliceride (TG) utilization in the presence of a acid or alkali catalyst is affected by high level of water content and free fatty acid (FFA) with undesirable saponified products. Hence the study to reduce catalyst has attracted interest in water-added supercritical method with a feature of easier product separation. The glycerol (side reaction in biodiesel process) is more soluble in water than in MeOH (Kusdiana & Saka, 2004; Georgogiannia *et al.*, 2008). Single phase medium using supercritical fluid (SCF) due to the creation of a single phase environment has some unique advantages including increased species mixing, heat and mass transfer, fast reaction typically at a few minutes level. These systems are environmentally benign, and have good scalability, as well as being simple and easy for continuous production. The SCFs is ideal for separation and extraction of useful products and for oxidation of organic materials (Wen, Jiang & Zhang, 2009). For most of the supercritical methods of biodiesel production, the reaction requires temperatures of 340– 400°C and pressures of 20–70 MPa. Rapeseed oil was treated at 250-350°C, 43 MPa and 240 s with a molar ratio of 42 in MeOH for transesterification to biodiesel fuel. By this MeOH approach, crude vegetable oil as well as its wastes could be readily used for biodiesel fuel production in a simple preparation. Regardless of the content of water supercritical MeOH method does not require a catalyst and the FFA in the oils are esterified at once (Kusdiana & Saka, 2004).

### 2.5.3 Co-solvent

Enhancing solubility, addition of a co-solvent is to create a single phase greatly accelerated the reaction so that it reached substantial completion in a few minutes (Royon *et al.*, 2007). The technique is applicable for use with other alcohols and for acid-catalyzed pretreatment of high free fatty acid feed stocks. Comparison of various co-solvent dimethyl ether (DME), diethyl ether (DEE), tert-butyl methyl ether (TBME) and tetrahydrofuran (THF) (Guan, Sakurai & Kusakabe, 2009) to synthesize biodiesel from sunflower oil by using a KOH catalyst at 25°C in a closed batch reactor was reported (Wen *et al.*, 2009). Addition of a co-solvent enhanced the transesterification rate at the MeOH/oil molar ratio of 6 at 25°C, and sunflower oil was almost completely converted into biodiesel after 20 min reaction while only approximately 78% conversion was reached in the absence of a cosolvent. The oil conversion was influenced by the cosolvent/ MeOH molar ratio, MeOH/oil molar ratio, and catalyst concentration. However, the homogeneous flow was broken with the formation of immiscible glycerol, and transformed to a dispersed flow of fine glycerol droplets. The problem of immiscibility of MeOH and vegetable oil leading to a mass-transfer resistance in the transesterification of vegetable oil (Kusdiana & Saka, 2004) can be overcome by this method amongst many other techniques being developed like membrane separation and inert dopant (Disselkamp *et al.*, 2006)

### 2.5.4 Microwave method

Microwave irradiation is a well-established methodology to improve extraction and accelerate chemical reactions such as those of hydrolysis and esterification (Ipsita & Gupta, 2003) because of its convenience, rapidity, and economy advances in equipment design, trends in electrical energy costs, and research on food properties have provided a basis for modeling microwave heating patterns that should stimulate the development of new and improved commercial food processes (Tan *et al.*, 2001).

In conventional heating of transesterification process (batch, continuous, and super critical MeOH process), heat energy is transferred to the raw material through convection, conduction, and radiation from surfaces of the raw material as shown

when triglyceride (TG) in soaked soybeans were already hydrolyzed into diglyceride (DG) and free fatty acids during soaking and were further hydrolyzed by microwaves. Satisfactory transesterification was achieved in a short time (30s), with alcohol to oil molar ratio 12:1 and the continuous conversion of waste frying palm oil to ethyl ester was over 97%. Although, the mechanism of the microwave effect on a chemical reaction, whether thermal or non-thermal, is debatable (Saifuddin & Chua, 2004), however the transesterification results clearly establish that there is considerable enhancement in reaction rates. This brings about considerable time saving as well as cost (Kusdiana & Saka, 2001). 100% biodiesel yield by applying microwave irradiation for two minutes compared to one hour with the conventional technique, with adjusted temperature to 65°C, a MeOH/oil molar ratio of 6:1and potassium hydroxide (1%) used as a catalyst has been reported (Refaat & El Sheltawy, 2008) and showed that microwave-enhanced biodiesel is not, at least, inferior to that produced by the conventional technique (Yoshida & Takagi, 1997)

### 2.5.5 Ultrasonic reactor method

An ultrasonic field is known to produce unique chemical and physical effects that arise from the collapse of the cavitation bubbles (Bondy & Sollner, 1935). Their uses have been cited in synthesis of nanostructured materials, processing of biomass, sonofusion, sonodynamic therapy, and sonochemical degradation of pollutants (Hanh *et al.,* 2007) and hazardous chemicals (Schuchardt, Sercheli & Vargas, 1998). A low frequency ultrasonic irradiation can be used to produce emulsions from immiscibility liquids and help generate small droplets and large interfacial areas if the ultrasonication device is placed near the liquid–liquid interface in a two phase reaction system (Bondy C & Sollner, 1935; Sivakumar *et al.,* 2002).

Disselkamp *et al.,* 2006, contrasted differences in a heterogeneous catalytic reaction for cavitating and non cavitating ultrasound incorporating an inert dopant, which does not partake in solution chemistry to enable facile transition from high power non cavitating to cavitating condition as not all liquid readily cavitation. The mechanism for discriminating between physical and chemical effects of ultrasound with different conditions have been coupled to a bubble dynamics mode (Kalva,

Sivasankar & Moholkar, 2009) and the result is attributed to the difference in intensity of microturbulence produced by cavitation bubbles in oil and MeOH. This effect is a low intensity of microturbulence generated by cavitation bubbles in oil, which restrict an intimate dispersion of oil in MeOH for high alcohol to oil molar ratios.

The optimum alcohol to oil molar ratio for the experimental system used in this study is 12:1. Transesterification of TG with various alcohols has been shown (Vasudevan & Briggs, 2008), under the low frequency ultrasonic irradiation (24KHz), stirring conditions (600 rpm). The optimal reaction condition was obtained with an alcohol to TG ratio of 6:1 (Hanh *et al.,* 2007) low frequency ultrasonication (24KHz) and mechanical stirring (600 rpm) with MeOH gave high yields of methyl esters (95%) after a short reaction time (20 min) similar to those using mechanical stirring. Use of ultrasonication in conventional transesterification with ethanol gave similar yields to those using mechanical stirring but significantly lower than respective yields using MeOH. This also showed the alcohol-dependency of the operation. Gogate, Tayal & Pandit, (2006) review presented this method as very efficient for intensification of chemical processing and the analysis, fabrication, design of cavitational reactors would offer realistic solution to conventional transesterification.



### 2.5.6 Oscillatory flow reactor for transesterification reaction

Oscillatory flow reactor (OFR) was first introduced by Harvey, Mackley & Seliger, (2003) to produce biodiesel through some improvement in mixing intensity between reactants. OFR is a novel type of continues flow reactor, consisting of tubes containing equally spaced orifice plate baffles. Therefore, an oscillatory motion is superimposed upon the net flow of the process fluid, creating flow patterns conducive for efficient heat and mass transfer, whilst maintaining plug flow regime (Harvey *et al.,* 2003).

In addition, each baffle essentially behaves as a stirred tank that lead to excellent mixing and suspension by creating vortices between orifice baffles and oscillating fluid (Zheng, Skelton & Mackley, 2007). This is an essential element in

designing a biodiesel reactor especially when heterogeneous catalysts are used due to the presence of three immiscible phases (oil–alcohol–catalyst) at the initial stage of reaction. Thus, improvement in mixing and suspension of catalysts tend to produce higher yield of biodiesel in a shorter reaction time compared to conventional batch-type stirred tank reactor.

Apart from that, OFR allows longer residence time as the mixing is independent of the net flow and hence the reactor length-to-diameter ratio can be reduced. This is an important plus point if the process is scaled up for commercial application in order to reduce the overall capital and pumping cost. Harvey *et al.,* (2003) applied OFR in the production of biodiesel from waste cooking oil and pure rapeseed oil. The reaction was performed at temperature of 20–70 °C, residence time of 10–30 min and molar ratio of methanol to oil was maintained at 1.5. Pure sodium hydroxide (32.4 g) was dissolved in pure methanol initially at 40°C for 1 h. It was found that at 50°C and 30 min of reaction time, nearly 99% of biodiesel was produced. Moreover, the product contains negligible amount of triglyceride and diglyceride. However, some traces of monoglyceride were detected (Noureddini & Zhu, 1997). Nevertheless, Harvey *et al.,* (2003) concluded that in-depth study on OFR in transesterification with heterogeneous catalyst is promptly required as OFR is ideal for suspending solid catalysts or polymer supported catalysts.

### 2.5.7 Mechanical stirring method

Several commercial processes for FAME production have been developed. In conventional (mechanical stirring method) industrial biodiesel processes, vegetable oil methanolysis is achieved using a homogeneous catalyst system operated in either batch or continuous mode. Sodium hydroxide or sodium methylate is often used as catalyst. Sodium is recovered after the transesterification reaction as sodium glycerate, sodium methylate, and sodium soaps in the glycerol phase.

In the mechanical stirring reaction, the temperature is 60-70$^{o}$C, and it takes about an hour and half for the reaction to proceed to completion (Ma & Hanna, 1999). The alcohol and the alkali metal hydroxide catalyst are first mixed before the reaction in a separate unit to form the metal alkoxide. The alcohol and the alkoxide

catalyst are then mixed with oil in the reactor. The reactor is a batch reactor with stirrer, or a continuous or semi-continuous stirred tank reactor. A condenser is used to condense the alcohol continuously. The boiling point of the alcohol is in the range of the reaction temperature. Oil and alcohol are immiscible; they are constantly stirred, and the reaction takes place at the interface of two phases. The reaction is described by second order reaction kinetics (Freedman, Butterfield & Pryde, 1986). The stoichiometric ratio of triglyceride and alcohol for the reaction is 3:1, but 6:1 molar ratio is the optimal molar ratio used to push equilibrium to one side for maximum biodiesel conversion (97~98 %) (Freedman *et al.*, 1986) and 0.5 wt % of catalyst is considered optimal for maximum activity.

#### 2.5.7.1 Drawbacks Mechanical stirring

Transesterification reactions involve reactions between WCO and methanol in the presence of a catalyst. WCO and methyl alcohol are immiscible liquids and form separate layers when mixed together in a reactor. However conventional transesterification reaction requires mixing continuously for long periods of time to facilitate the reaction between oil and alcohol, due to the reaction can takes place only in the interfacial region between the two liquids. Therefore, this mixture is sonicated, ultrasonic waves produce cavitation at these interfacial areas. As a result, an emulsion of oil and alcohol forms, providing large surface areas for reaction. It is observed that reaction time is reduced significantly

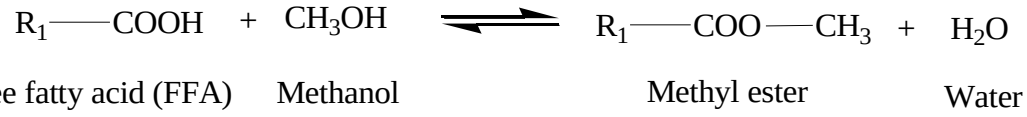
## 2.6 The biodiesel process

### 2.6.1 Esterification process

Esterification, as it applies to biodiesel production, is the chemical reaction by which a fatty acid, typically a free fatty acid in degraded or second-use oil, reacts with an alcohol to produce an alkyl ester and water. The process differs from the

transesterification reaction in that the reaction is occurring directly between the alcohol and the fatty acid molecule. The intermediate steps of cleaving the fatty acid chains from the glycerin backbone are not present. For this reason, no glycerin is produced during the esterification reaction (Altic, 2010).

The following formula shows the basic esterification reaction with methanol. A fatty acid molecule reacts with a methanol molecule to form a methyl ester plus a water molecule:




The above formula was adopted from Deshmane, Gogate & Pandit, (2009) and represents the basic chemical reaction for all industrial esterification reactions using methanol as the alcohol

Conventionally, virgin vegetable oils and high-grade animal fats are the feedstock of choice for biodiesel production due to low levels of impurities, such as free fatty acids and sulfated proteins, which can cause problems with processing and final product quality. Rapeseed alone comprises of roughly 84% of the lipid stocks used for biodiesel production. By comparison, sunflower and palm oil each represent 13% of the feedstocks with soybean trailing with a 1% share. All other feedstock such as waste cooking oils, animal fats, jatropha, peanut, mustard, etc. make up the remaining 2% (Pahl, 2005). Second use oils such as yellow or brown grease are thermally or chemically degraded waste oils that primarily contain grease collected from restaurant or industrial grease traps. Most of this oil is spent cooking oil from restaurants that has been thermally degraded by sustained high temperatures. It further degrades when in contact with water in the grease trap through a process known as hydrolysis. This degradation produces molecules known as free fatty acids. Fatty acids will chemically react with the typical alkaline catalysts used in base catalyzed biodiesel reactions to form soap. Free fatty acids are always present in oils, however mass concentrations above 4% will generate more soap than can be dealt with reasonably in a conventional base-catalyzed reaction and will prevent the reaction from going to completion in almost all cases. (Tyson, 2002)

### 2.6.2 Transesterification reaction

The chemical reaction by which a lower alcohol reacts with a triglyceride to yield a fatty acid alkyl ester is known as transesterification. It occurs easily with the lower alcohols such as methanol or ethanol. The process is slow under normal conditions without the presence of a catalyst. Traditionally, an alkaline catalyst such as sodium or potassium hydroxide is used to catalyze and accelerate the reaction at standard temperatures and pressures. The catalytic reaction is complicated; however the necessity for a catalyst arises from the relative insolubility of alcohol in oils. Catalysts provide a phase-transfer as well as an ion exchange effect which reduces reaction times by many orders of magnitude (Mittelbach & Remschmidt, 2004).

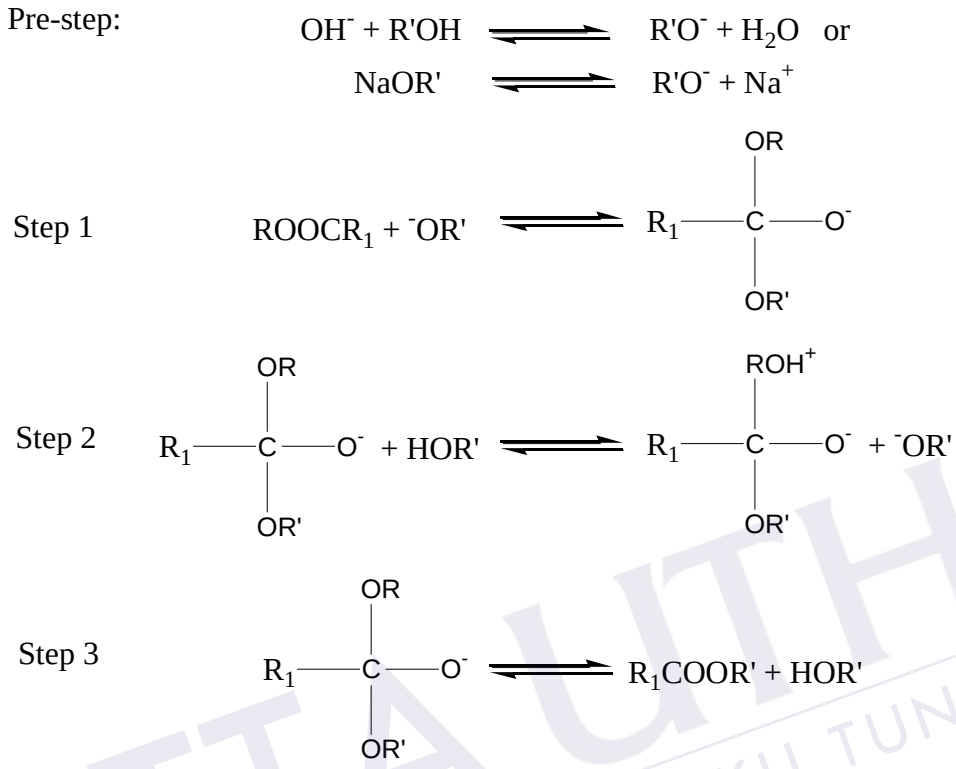
Transesterification consists of a number of consecutive, reversible reactions (Schwab, Bagby & Freedman, 1987; Freedman *et al.*, 1986). The triglyceride is converted stepwise to diglyceride, monoglyceride and glycerol (Figure 2.2). A mole of ester is liberated at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol.

$$\text{Triglyceride (TG)} + \text{R'OH} \rightleftharpoons \text{Diglyceride (DG)} + \text{R'COOR}_1$$
$$\text{Diglyceride (DG)} + \text{R'OH} \rightleftharpoons \text{Monoglyceride (MG)} + \text{R'COOR}_2$$
$$\text{Monoglyceride (MG)} + \text{R'OH} \rightleftharpoons \text{Glycerol (GL)} + \text{R'COOR}_3$$

Figure 2.2: The transesterification reactions of vegetable oil with alcohol to esters and glycerol. (Freedman *et al.*, 1986)

The reaction mechanism for alkali-catalyzed transesterication was formulated as three steps (Eckey, 1956). The first step is an attack on the carbonyl carbon atom of the triglyceride molecule by the anion of the alcohol (methoxide ion) to form a tetrahedral intermediate. In the second step, the tetrahedral intermediate reacts with an alcohol (methanol) to regenerate the anion of the alcohol (methoxide ion). In the last step, rearrangement of the tetrahedral intermediate results in the formation of a fatty acid ester and a diglyceride. The catalyst such as NaOH, KOH, $K_2CO_3$ or other similar catalysts were mixed with alcohol and alkoxide group is formed (Sridharan & Mathai, 1974). A small amount of water, generated in the reaction, may cause soap

formation during transesterification. Figure 2.3 summarizes the mechanism of alkali-catalyzed transesterication.




where R-OH diglyceride, $R_1$ long chain alkyl group, and R' short alkyl group

Figure 2.3: The mechanism of alkali-catalyzed transesterification of triglycerides with alcohol. (Eckey, 1956)

## 2.7 Variables influencing the transesterification reaction

### 2.7.1 Molar ratio of vegetable oil to methanol

Methanol is a commonly used alcohol for transesterification because of its low price and highly reactive nature (Lang *et al.*, 2001). The stoichiometric ratio required for transesterification is 1:3 moles of vegetable oil to alcohol. However, it has been found that the molar ratio of vegetable oil to alcohol depends on the type of catalyst used for the reaction. For example, the molar ratio of 1:6 moles of soybean oil to

methanol has been found to be the most suitable in the case of alkali-catalyzed transesterification because an excess of alcohol is required to drive the reaction (Freedman *et al.*, 1986). For acid-catalyzed transesterification, a 1:30 vegetable oil to alcohol ratio is generally used (Freedman, Pryde & Mounts, 1984).

### 2.7.2 Moisture contents

Water content promotes the formation of soap during the reaction and reduces catalyst efficiency. The presence of water in acid catalyzed transesterification reduces the percentage of biodiesel produced to a greater extent compared to an alkaline catalyst. For example, in a reaction mixture of soybean oil, methanol and sulfuric acid, 0.5% water content reduces the resultant biodiesel conversion from 95% to 90% (Canacki & Van Garpen, 1999).

### 2.7.3 Free fatty acid

For an alkali catalyzed transesterification reaction, vegetable oil should not contain any free fatty acids. If any free fatty acids are present in the vegetable oil, an alkaline catalyst (e.g. NaOH) is utilized in neutralizing these free fatty acids which only consumes the catalyst and slows down the reaction. The acid value of glycerides should be less than 1 for a NaOH catalyzed transesterification reaction (Wright *et al.*, 1944). Acid value is the milligrams of potassium hydroxide (KOH) required for neutralizing the free fatty acids present in 1 g of vegetable oil.

### 2.7.4 Catalyst

Transesterification reactions can occur in the absence of catalysts, (Diasakou, Louloudi & Papayannakos, 1998) however, it requires high temperature, pressure and long reaction times. If all these requirements are met, the process cost is

relatively high. This method produces relatively high purity esters and soap-free glycerol, but because it is un-economical, it is typically not considered for industrial production of biodiesel. Three types of catalysts are generally used for biodiesel production: alkaline catalysts, acidic catalysts, and enzymes.

### 2.7.4.1 Alkaline catalysts

Alkaline catalysis is the most commonly used process for biodiesel production. Its main advantage is that a high ester yield is obtained in short reaction times under mild reaction conditions (Canacki & Van Garpen, 1999). However, alkaline catalysts are highly sensitive to free fatty acids in vegetable oils. Therefore only low acidic vegetable oils produce high ester yields after transesterification. However, de-acidification of vegetable oil prior to transesterification reduces this issue. Examples of alkali catalysts are: sodium hydroxide, potassium hydroxide, alkali metals (such as sodium), alkali metal carbonates (such as sodium carbonate, and potassium carbonate).

### 2.7.4.2 Acidic catalysts

Acid–catalyzed transesterification requires a relatively high temperature (~100 °C), pressure (~5 bars) and large amounts of alcohol. It is also slower in comparison to alkaline catalysis. The only advantage of this type of catalytic conversion is that it can efficiently esterifies free fatty acids in vegetable oils and is therefore used to transesterify high free–acid–containing feedstock, such as waste edible oil (Mittelbach & Remschmidt, 2004).

#### 2.7.4.3 Enzymes

Enzymes or lipases extracted from microorganisms can also be used as catalysts for the transesterification reaction (Mittelbach & Remschmidt, 2004). The advantages of these biocatalysts are:

(a) Biodiesel conversion under mild temperature, pressure, and pH conditions.
(b) No catalyst residues or soap in the final product.
(c) High quality glycerol is produced.
(d) These catalysts efficiently esterify free fatty acids and thus can be used for transesterification of oils or fats containing high free fatty acid contents.

The disadvantages of these catalysts include:

(a) Long reaction times and higher catalyst concentrations are required.
(b) These catalysts are expensive and not economical for commercial use.
(c) Enzymes are typically difficult to remove from the final products (i.e., biodiesel and glycerol) after the reaction is complete.

### 2.7.5 Reaction temperature

Temperature has no detectable effect on the ultimate conversion to ester. However, higher temperatures decrease the time required to reach maximum conversion (Pinto *et al.,* 2005). Transesterification can be conducted at various temperatures ranging from room temperature to the boiling point of the alcohol employed (68$^{o}$C in case of methanol) so that the reactor does not need to be pressurized. Thus, the usual temperature used during transesterification in most literature is 60-65°C. When the reaction temperature closes or exceeds the boiling point of methanol (68 °C), the methanol will vaporize and form a large number of bubbles which may inhibit the reaction.

### 2.7.6 Reaction time

Freedman *et al.*, (1984), found that the conversion rate of fatty acid esters increases with reaction time. At the beginning, the reaction is slow due to the mixing and dispersion of alcohol into the oil. After a while, the reaction proceeds very fast. Normally, the yield reaches a maximum at a reaction time of < 90 min, and then remains relatively constant with a further increase in the reaction time (Leung & Guo, 2006; Freedman *et al.*, 1984). Moreover, excess reaction time will lead to a reduction in the product yield due to the backward reaction of transesterification, the result in a loss of esters as well as causing more fatty acids to form soaps (Eevera, Rajendran & Saradha, 2009; Freedman *et al.*, 1984).

## 2.8 Biodiesel production using ultrasonic technique

Ultrasonic technology has been recognized as an effective method to enhance mass transfer rate between immiscible liquid–liquid phases within a heterogeneous system (Ji *et al.*, 2006). Therefore, it has been widely used in various biological and chemical reactions to improve the yield within a shorter reaction time. Ultrasound is defined as sound with frequency beyond human ear can respond. The normal sound frequency that can be detected by human lies between 16 and 18 kHz, but frequency for ultrasound generally lies between 20 kHz and 100 MHz (Vyas, Verma & Subrahmanyam, 2010). This high frequency sound wave will compresses and stretches the molecular spacing of a medium in which it passes through. Thus, molecules will be continuously vibrated and cavities will be created. As a result, micro fine bubbles are formed through sudden expansion and collapse violently, generating energy for chemical and mechanical effects (Colucci, Borrero & Alape, 2005). Furthermore, the collapsed bubbles will disrupt the phase boundary and impinging of the liquids to create micro jets, leading to intensively emulsification of the system (Ji *et al.*, 2006).

Ultrasonic technology in transesterification has proven to be an efficient mixing tool and provides sufficient activation energy to initiate the reaction (Singh, Fernando & Hernandez, 2007). Ultrasonic-assisted transesterification does not only

shorten reaction time, but also minimize the molar ratio of alcohol to oil and reduce energy consumption compared to conventional mechanical stirring method (Vyas *et al.*, 2010). However, up to now, there are only few studies applying ultrasonic technology in transesterification of waste cooking oil (Refaat & El Sheltawy, 2008).

Stavarache, Vinatoru & Maeda, (2007) analyzed the use of ultrasound for biodiesel production on a variety of oil types. Using KOH base catalyst and methanol in glass flasks, the reactions were driven via an ultrasonic cleaning bath filled with water. This approach allowed for temperature control. The results indicated that under ultrasound, the limiting step in the reaction changed from the classical case. Instead of the reaction from diglycerides to monoglycerides as the rate limiting step, it was reported that the MG to glycerol step became the limiting factor. Controlling the temperature of the reaction was an improvement to other studies, however the interface created by the water in the ultrasonic bath and the glass reaction likely dissipated the majority of ultrasonic energy generated.

Singh *et al.*, (2007), reported studies utilizing ultrasonic for base catalyzed transesterification. The experiments utilized soybean oil, methanol, and potassium hydroxide catalyst in a power adjustable ultrasonic reactor. Authors claim improved yields compared traditional methods, yet perform no reaction rate calculations. The ultrasonic frequency used was 28 kHz with powers varying from 79 to 131 kW. The reaction time for 98% yield of methyl esters was reported to be 5 minutes. The authors claim that the reaction yields decrease with increasing power. The correlation of ultrasonic power in this study was misleading. The results show that the reaction temperatures increased with increasing power, which is known to decrease the amount of power delivered from a cavitation collapse.

Wu *et al.*, (2007) recently published a unique study regarding the dispersed droplet size of ultrasonically formed biodiesel mixtures. The authors measured droplet size using light scattering techniques for both rotary mixed and ultrasonically mixed biodiesel reactant emulsions. The results showed that ultrasonic techniques produced smaller droplets that standard mixing. This study was the first to discuss the mixing effect of ultrasound in the biodiesel process. However, the authors used surface active emulsion stabilizers, which limit the applicability of dispersed phase droplet size.

## 2.9 Ultrasonic cavitations

The important effects of high intensity ultrasonics for this study are cavitation, atomization, streaming, and jetting. Each aspect is believed to be a component of ultrasonic emulsification, among other potential processes (Kropf, 2008).

Cavitation is the phenomenon of the generation of large numbers of micro bubbles (cavities) in a liquid when a negative pressure is applied. When sound waves propagate through a liquid medium, they generate compression and rarefaction regions in the liquid. The intermolecular distances between the liquid molecules also expand and contract along these waves. At very low pressure in the rarefaction region, the intermolecular spaces exceed the critical molecular distance and the liquid tears apart to form void spaces or micro bubbles. These micro bubbles oscillate with the wave motion and grow in size by taking in vapor from the surrounding liquid medium and by aggregating with other micro bubbles (Mason, 1999). Within a few cycles they grow to an unstable size and collapse violently, releasing large amounts of energy and creating localized temperatures of up to 5000 K (Flint & Suslick, 1991). The growth and subsequent collapse of cavitation bubbles is shown in Figure 2.4. The bubble collapse produces high shear forces which mix the liquid vigorously and fracture nearby particles.

The ultrasonic mixing effect is not due to acoustic streaming; however it is debated as to whether the effect is derived from cavitations disruption at an interface or capillary wave atomization (Kropf, 2008). In the opinion of this author, both effects occur in during ultrasonic emulsification. The dominant phenomenon appears to be that which produces the most stable emulsion. In these terms, most stable is to mean smallest dispersed phase droplet sizes. So if two competing emulsification effects are occurring, the one resulting in smaller droplets will dominate as it would reduce the larger droplets. Nevertheless, to obtain a notion of the effect of ultrasonic power and frequency both cases must be considered.

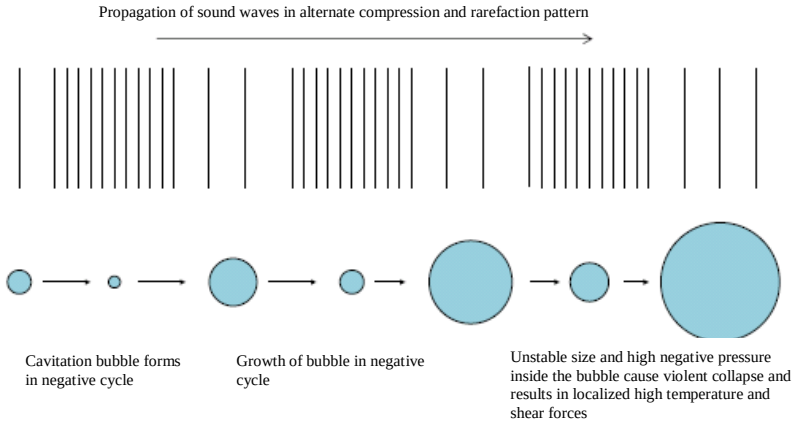



Figure 2.4: Growth and collapse of cavitation bubble in a liquid medium when ultrasonic waves are applied. (Kropf, 2008)

# CHAPTER 3

# METHODOLOGY

## 3.1 Materials and equipments

### 3.1.1 Materials

WCO was collected from a local Malaysian potato crackers factory. It was then filtered through normal sieve to remove any suspended food particle and then heated to evaporate water residue in it. As the free fatty acid contents in the WCO obtained was observed to be very little (less than 2%), the WCO was used directly. Methanol pure analytic grades (p.a), sodium hydroxide (NaOH) (p.a), potassium hydroxide (p.a), phenolphthalein indicator (p.a), ethanol (p.a) were purchased from HmbG Chemical Company Malaysia. Another chemical such as heptanes (p.a), Pyridine (p.a), MSTFA (N-methyl-N-trimethylsilyl trifluoroacetamide), Glycerin, 1-Mono [cis-9-octadecenoyl]-rac-glycerol (monoolein), 1,3-Di [cis-octadecenoyl] glycerol (diolein), 1,2,3-Tri [cis-octadecenoyl] glycerol (triolein), (S)-(−)-1,2,4-Butanetriol (Internal Standard 1), 1,2,3-Tridecanolylglycerol (tricaprin) (Internal Standard 2), and methyl heptadecanoate were supplied from Sigma Aldrich Malaysia.

### 3.1.2 Equipments

The ultrasonic tubular reactor type MSG.1200.IX-LF and conventional ultrasonic cleaner laborette 17 are shown in Figure 3.1 and Figure 3.2, respectively. It used to perform the transesterification reaction from waste cooking oil. The specification of ultrasonic tubular reactor have diameter 60 mm x 580 mm length with quick flanges and covers (material SS316L), maximal output ultrasonic power 1300 W and adjustable frequency range 17.5 kHz to 28.5 kHz. Meanwhile, ultrasonic cleaner Laborette 17 has specification as follows: diameter 24.5 cm, 13 cm deep, 5.6 liters capacity and fixed frequency at 35 kHz.

The mechanical stirring method was conducted in three-neck flask, magnetic stirrer, condenser and water bath. The reaction temperature and stirring speed were controlled by digital hotplate and mercury thermometer, respectively.

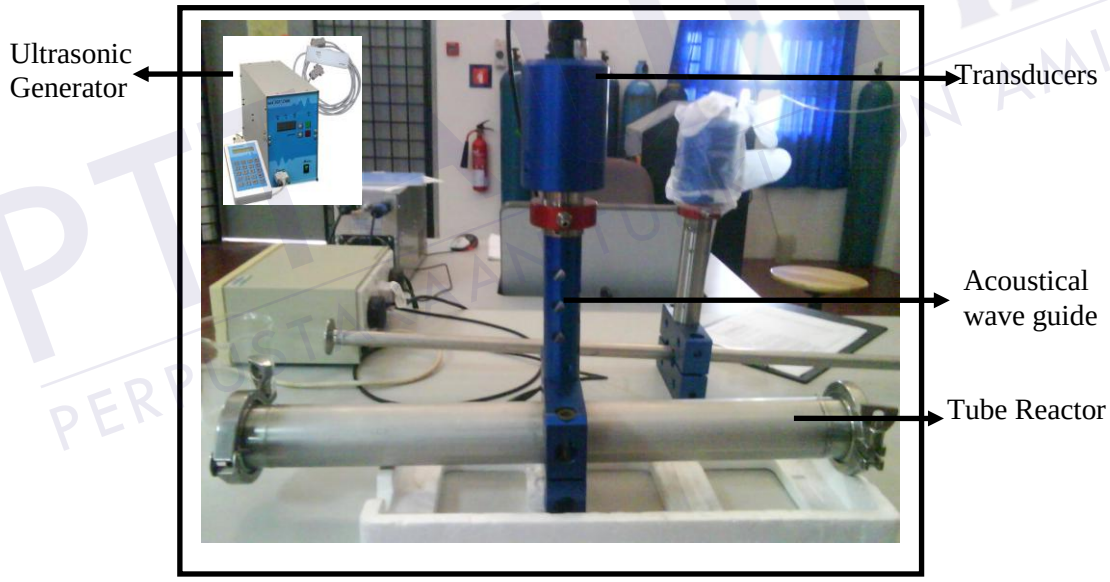



Figure 3.1: Experimental set-up of ultrasonic clamp on tubular reactor for biodiesel process.

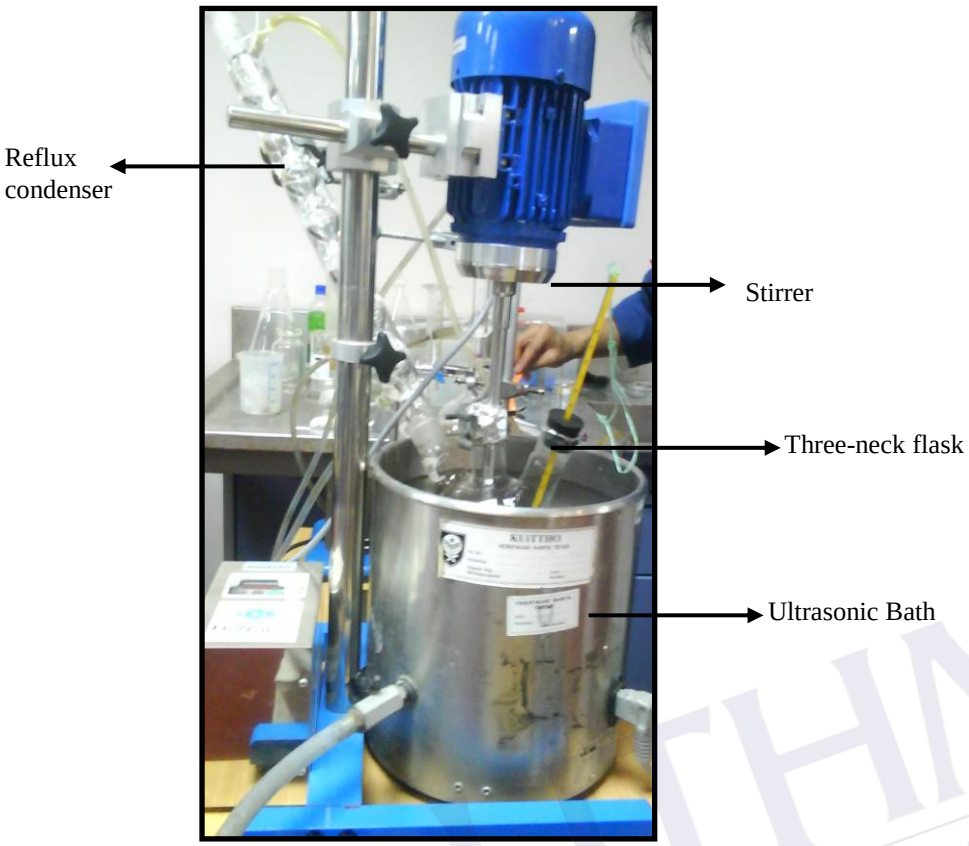



Figure 3.2: Experimental set-up of conventional ultrasonic cleaner for biodiesel process.

## 3.2 Experimental procedure

There were five stages in the experimental procedure. The breakdown of experimental procedure is shown in Figure 3.3. The first stage was the process of preparation sample, the second stage was to produce the synthesize of WCO to FAME using ultrasonic tubular reactor, the third stage was the process of liquid-liquid equilibrium (LLE) based on the second stage, the fourth stage was to compare the ultrasonic tubular reactor with conventional ultrasonic cleaner and mechanical stirring. The fifth stage was the process of semi continuous ultrasonic tubular reactor at 15 kg WCO.

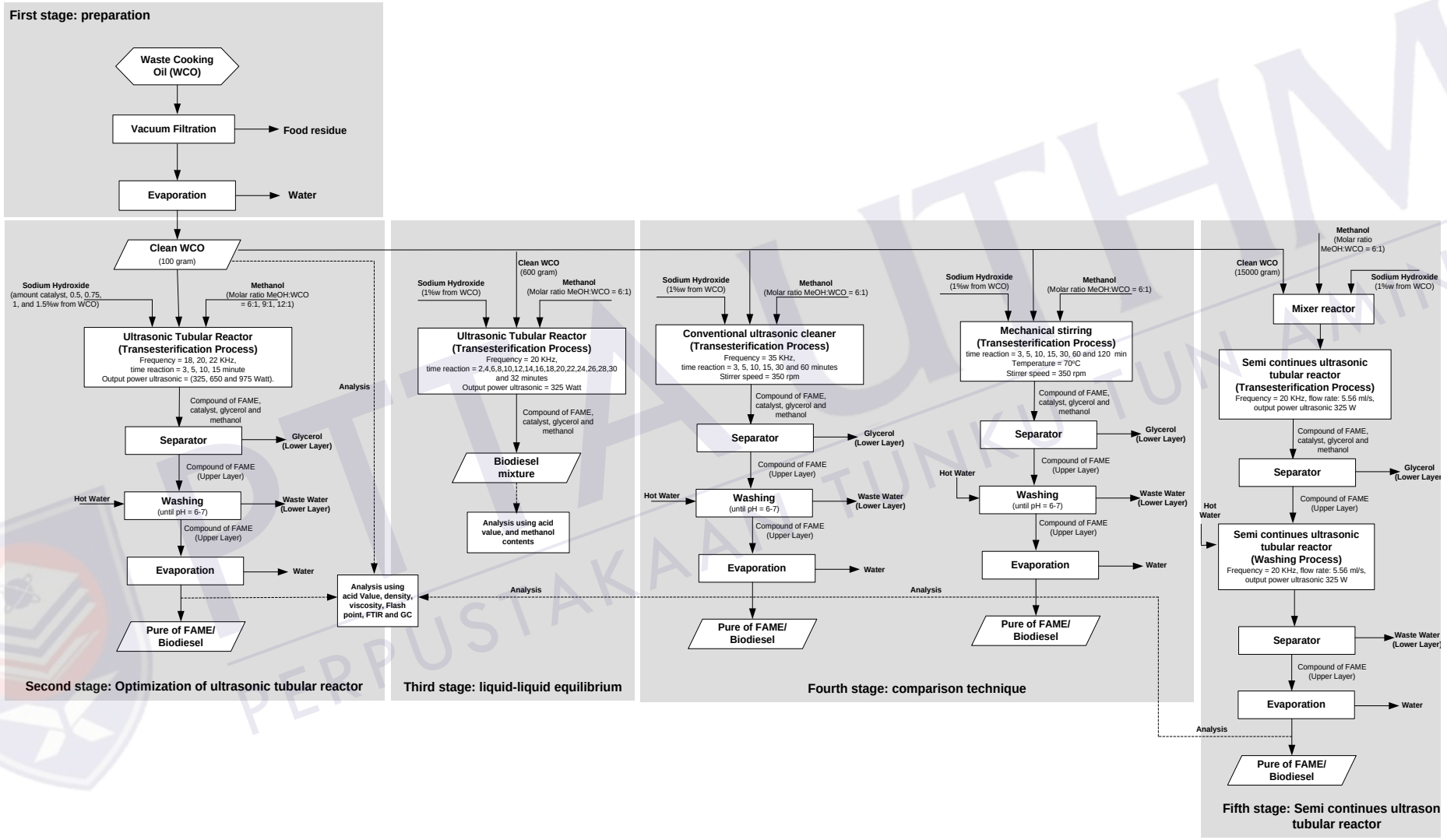



Figure 3.3: Experimental flowchart biodiesel production based on WCO comprises first stage, second stage, fourth stage and fifth stage.

### 3.2.1 First stage: Preparation sample

The WCO must be filtered to remove food residues by vacuum filter. Filtered WCO was dried at 110$^{o}$C for 30 min by oven Memmert Model UNP 700. Acid value was determined by method AOCS Ca5a-40 to estimate the free fatty acid content.

### 3.2.2 Second stage: Optimization of ultrasonic tubular reactor

The experiment was carried out using an ultrasonic tubular reactor which it is included mastersonic software for control the ultrasonic parameter. Ultrasonic tubular reactor with frequency of 20 kHz was arranged on display ultrasonic generator. 100 g of WCO per batch was added in the reactor. The powder of NaOH first dissolved completely in methanol (MeOH) and then the mixture of MeOH – NaOH was added to the tubular reactor. The calculation molar ratio was shown in Appendix B. As soon as the mixture of MeOH – NaOH was added to the WCO, the time was noted and the reaction was carried for about 5 minutes. After completion in 5 minutes, the mixture was transferred into a separator tunnel for phase separation. The biodiesel mixture formed at the upper layer and glycerol form in the lower layer. The traces of catalyst and MeOH in biodiesel layer were washed out by warm water until pH 6-7. Finally, the biodiesel layer was dried by oven and analyzed.

Different operating parameters were used in this research, by optimizing the ester contents of WCO based on reaction time at 3, 5, 10, and 15 minute, including WCO to MeOH molar ratio at 1:6, 1:9, and 1:12, the amount of catalyst (0.5%wt, 0.75%wt, 1 %wt and 1.25%wt based on WCO), the ultrasonic frequency were 18 kHz, 20 kHz and 22 kHz and the output power ultrasonic were 325 Watt, 650 Watt and 975 Watt.

### 3.2.3 Third Stage: Liquid-liquid equilibrium (LLE)

During the transesterification, the time raection of three main components including MeOH, FAME and WCO, was characterized with the ternary phase diagram of WCO–FAME–MeOH. The LLE experiments for this ternary system were carried out using an ultrasonic tubular reactor at atmospheric pressure and 30-34$^{o}$C based on optimum condition in first stage. The experiments were performed in a tube reactor of 600 gram WCO. During the reaction, samples of 30 ml were taken at the following reaction times: 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32 and 34 min. Measurements of the boundary of LLE were carried out by acid value analysis and methanol content based on GC method.

### 3.2.4 Fourth Stage: Comparison of ultrasonic tubular reactor between conventional ultrasonic cleaner and mechanical stirring

The experiment was performed by conventional ultrasonic cleaner and mechanical stirring. The optimized parameter from ultrasonic tubular reactor was applied to conventional ultrasonic cleaner and mechanical stirring. Experimental procedures for conventional ultrasonic and mechanical stirring were similarly adopted (second stage) for ultrasonic tubular reactor method. The end of reaction time in conventional ultrasonic cleaner and mechanical stirring was used in 60 and 120 minute, respectively. During the reaction, samples of 30 ml each were taken at the following reaction times: 3, 5, 10, 15, 30, 60, and 120. The conversion of WCO to FAME was carried out by acid value analysis.

### 3.2.5 Fifth Stage: Semi continuous ultrasonic tubular reactor

Based on the optimum process of the second stage, the reaction was performed by semi continuous ultrasonic tubular reactor. The mixer was initially process with the mixture of WCO (15 kg) and methanol, placed in the constant-temperature (40$^{o}$C)

with its equipment, and then heated to a predetermined temperature. The example of calculation was shown in Appendix B. NaOH (150 g) was dissolved in the 3.26 kg (ratio mole MeOH to WCO is 6:1), and the mixture was added to the mixer. After that opened the main valve in the mixer until ultrasonic tubular reactor was full with mixture. The reaction was timed as soon as the valve output ultrasonic tubular reactor was opened and continued until the solution in mixer was empty. The flow rate of fluid is kept constant at 5.56 ml/s (based on calibration with refined palm oil). After completion, the mixture was transferred into a separator reactor for phase separation. The biodiesel mixture formed at the upper layer and glycerol form in the lower layer. The traces of catalyst and MeOH in biodiesel layer were washed by water using semi continuous ultrasonic tubular reactor until pH 6-7 and 5.56 ml/s of flow rate. Finally, the biodiesel layer was dried to elimination of water and methanol by mixer during 1 hour. After that, the samples were analyzed to determine chemical and physical properties.

## 3.3 Analysis of chemical properties

### 3.3.1 Free fatty acid value determination

Acid value (Av) is one of important indicator of vegetable oil quality. Av is expressed as the amount of KOH (in milligrams) necessary to neutralize free fatty acids contained in 1 g of oil (Firestone, 1996).

The Av determination was adopted from the method of Firestone (1996) started in the 0.1 g of oil, fatty acid or reaction product mixture (according to the expected acid value) was weighed in glass vial and dissolved in at least 25 ml of the solvent mixture. 5 drops of indicator was added to the glass vial mixture. It was then titrated, with the KOH solution (0.1 N) in a 10 ml burette to the end point of the indicator, the pink color persisting for at least 10 s. Free fatty acid percentage was converted to acid value by multiply the free fatty percentage by 1.99 (as palmitic). The free fatty acid content (% by wt) is calculated by the formula (AOCS Ca5a-40, 1996):

$$\text{Free fatty acids as palmitic, \%} = \frac{\text{mL of alkali x N x 25.6}}{\text{wt of sample}} \quad (3.1)$$

N= Normality of alkali

### 3.3.2 Attenuated Total Reflection Infrared Spectroscopy (ATR-IR) analysis

An Attenuated Total Reflection accessory operates by measuring the changes that occur in a totally internally reflected infrared beam when the beam comes into contact with a sample. An infrared beam is directed onto an optically dense crystal with a high refractive index at a certain angle. This internal reflectance creates an evanescent wave that extends beyond the surface of the crystal into the sample held in contact with the crystal. It can be easier to think of this evanescent wave as a bubble of infrared that sits on the surface of the crystal. This evanescent wave protrudes only a few microns (0.5 μ - 5 μ) beyond the crystal surface and into the sample (Perkin Elmer, 2005). Consequently, there must be good contact between the sample and the crystal surface. All sample collection and spectra data processing is handled using spectrum express software.

Figure 3.4: Instrument of Attenuated Total Reflection Infrared spectroscopy (ATR-IR) model Perkin Elmer Spectrum 100

The attenuated energy from each evanescent wave Attenuated Total Reflection Infrared spectroscopy (ATR-IR) is often used for rapid analyze of quality control. ATR-IR measurements were performed in a Perkin Elmer Spectrum 100 and used software spectrum express (Figure 3.4). The resulting vibration spectrum displays the "fingerprints" of functional groups narrowly and intensely in the IR region (4000-650 $cm^{-1}$). The formation of FAME group was determined in 1300 to 1060 $cm^{-1}$ spectral region (Siatis *et al.*, 2006)

### 3.3.3 Gas Chromatography analysis

Gas Chromatography (GC) as in Figure 3.5 is based on the principle that components, when carried by a carrier gas through a chromatography column, different in retention times. The difference in retention time is due to difference in molecular size and the interaction of the components with the column. A longer molecule tends to take more time than a shorter molecule to elute. A polar component tends to have a shorter retention time than a comparable non polar compound if the column coating is non-polar. The column can also be temperature programmed to analyze a range of components.

Figure 3.5: Instrument analytic of gas chromatography includes headspace autosapler model Perkin Elmer Clarus 500.

#### 3.3.3.1 Total glycerol, diglycerol (DG), monoglycerol (MG), triglycerol (TG) contents determination

This includes the free glycerol and the bound glycerol. Bound glycerol is a function of the residual amount of the triglycerides (TG) and partial glycerides (monoglycerides and diglycerides) that remain in the final biodiesel product (Foglia *et al.,* 2004). The amount of free glycerol is largely dependent on the production and the separation process. High values of free glycerol could be attributed to improper purification methods and also the hydrolysis of partial glycerides such as the MG, DG, etc. Bound glycerol is affected by factors such as incomplete transesterification reaction and moreover oils naturally contain MG, DG as constituent. High levels of total glycerol are the source of carbon deposits in the engine because of incomplete combustion (Knothe, 2001).

Sample was used after final washing and drying which the composition of TG, DG, MG and total glycerol was analyzed using a Perkin Elmer Gas Chromatography (GC) Model Clarus 500 (Figure 3.5), equipped with a DB-5 HT capillary column (0.53 mm x 5 m) J&W Scientific. The following condition of GC are : the column temperature was started at 50°C and held for 1 min, programmed 1 at 15°C/min up to 180°C, programmed 2 at 7°C/min up to 230°C, programmed 3 used at 10°C/min up to 370 °C, final temperature was held for 5 min, detector temperature at 380°C, carrier gas pressure (hydrogen) at 80 kPa, volume injected of 1 µl. The percentage (m/m) of total glycerol in the sample was calculated using the formula (EN 14105, 2003b):

$$GT = G + 0.255\ M + 0.146\ D + 0.103\ T \qquad (3.2)$$

where,

GT is the percentage (m/m) of total glycerol (free and bound) in the sample;

G is the percentage (m/m) of free glycerol in the sample;

M is the percentage (m/m) of monoglycerides in the sample;

D is the percentage (m/m) of diglycerides in the sample;

T is the percentage (m/m) of triglycerides in the sample.

### 3.3.3.2 Total ester contents determination

The quality of biodiesel define is total ester contents. Limits have been established by the American society for testing and materials (ASTM) and the European normalization (EN). They define the minimum to be 96.5 %wt for fatty acid methyl esters. This is the most important component of biodiesel. The amount of esters in the final product is affected mainly by the extent of transesterification reaction.

In this research, biodiesel samples were analyzed using a gas chromatography (Perkin Elmer GC Model Clarus 500) equipped with a DB-5 HT capillary column (0.53 mm x 5 m) J&W Scientific. The analytic conditions for ester contents were as follow: the column temperature used 210$^{o}$C, temperature flame ionization detector (FID) of 250$^{o}$C, pressure of 80 kPa, flow carrier gas of 1 ml/min, temperature injector of 250$^{o}$C, split flow rate of 50 ml/min, time for analysis 20 minute and volume injected of 1 µl. The ester contents (C), expressed as a mass fraction in percent, is calculated using following formula (EN 14103, 2003a):

$$C = \frac{(\sum A) - A_{EI}}{A_{EI}} x \frac{C_{EI} x V_{EI}}{m} x 100\% \qquad (3.3)$$

where,

$\sum A$ is the total peak from the methyl ester in $C_{13}$ to that in $C_{24:1}$

$A_{EI}$ is the peak area corresponding to methyl heptadecanoate

$C_{EI}$ is the concentration, in milligram/milliliters of the methyl heptadecanoate solution

$V_{EI}$ is the volume, in milliliters, of methyl heptadecanoate solution

m is the mass, in milligrams of the sample

### 3.3.3.3 Methanol content determination

Some amount of the alcohol used in the transesterification reaction can remain in the final product after the reaction. High alcohol content in biodiesel pose safety risks especially during transportation and may cause deterioration of rubber components of the vehicles fuel system (Paraschivescu *et al*., 2007). The alcohol in biodiesel is indicated by its flash point; the lowest temperature at which application of an ignition

source causes the vapours of a specimen to ignite under the specified conditions of the test.

A reference sample of FAME can be prepared by extraction with water to ensure low methanol content, taking 30 ml of biodiesel and extracting four times with 10 ml of water. Then, the extracted biodiesel layer must be dried with $MgSO_4$ for 15 minutes, and analyzed using the parameters reported below. This prepared sample has to provide methanol content less than 0.001% m/m. Such a reference FAME can also be obtained from various commercial sources. In this study, raw waste cooking oil has been used, featuring very low methanol content. Using the reference FAME, three calibration solutions (A, B and C) were prepared by adding pure methanol to obtain concentrations of 0.5, 0.1 and 0.01% m/m respectively. Two ml from each calibration solution and unknown biodiesel sample were transferred into headspace vials, which were tightly crimped in order to prevent leaking.

The analytic procedure were follow: split flow of 100 ml/min, oven temperature of 160°C, carrier gas helium of 1.5 ml/min, temperature FID of 250°C, oven program of 50°C (1 min) to 130°C, increased every 10°C/min, final temperature oven must be hold 0.5 min. Set up a headspace autosampler, there are incubation temperature of 80°C, incubation time 40 min, Syringe temperature of 85°C and injected amount of 500 µl (EN 14110, 2003c) .

## 3.4 Analysis of physical properties

### 3.4.1 Kinematic viscosity determination

The kinematic viscosity of the WCO and biodiesel was determined using Hydromation Viscolite 700 (Figure 3.6). This test method involves measuring the temperature conducted with water bath for control the temperature ($40^{o}$C). To each viscometer, 50ml of biodiesel were added. For each viscometer, the fluid was drawn into the capillary tube. Each of the second time values was multiplied by the corresponding viscometer's calibration constant, yielding four values of kinematic viscosity. The mean of these two values was reported as the kinematic viscosity of biodiesel sample.

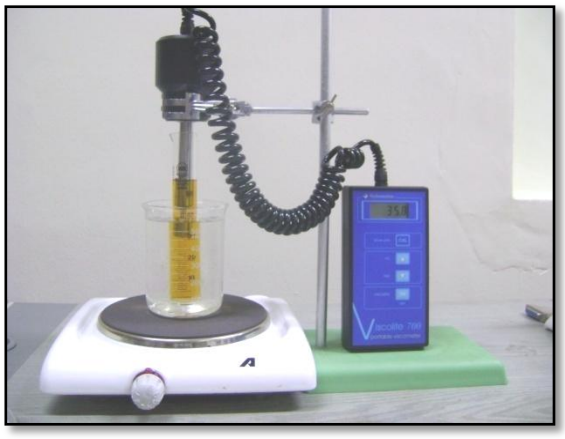


Figure 3.6: Instrument analysis of kinematic viscosity model Hydromation Viscolite 700

### 3.4.2 Flash point determination

The flash point temperature is one of the value measures of the tendency of the test specimen to form a flammable mixture with air under controlled laboratory conditions. It is only one of a number of properties which must be considered in assessing the overall flammability hazard of a material. The flash point was determined by the Pensky-Martens closed cup method (Figure 3.7) referred to ASTM D 93-08

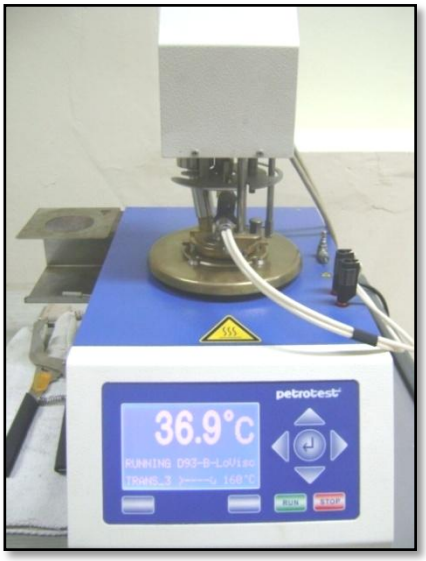



Figure 3.7: Instrument analysis of flash point using Pensky-Martens closed cup

### 3.4.3 Density determination of liquids by Gay-Lussac Pycnometer

The density (ρ) is elementary physical property of matter. For a homogeneous sample it is defined as the ratio of its weight to its volume. Density can be determined by Gay-Lussac Pycnometer as shown in Figure 3.8. The observation was started with washing input the pycnometer and cleaned with alcohol. After drying, the pycnometer was weighed with a digital balance, and distilled water was filled into the pycnometer until up to the marking point, and closed. The same procedure was used to measure the biodiesel and WCO. The density value is calculated using formula in the below:

$$\rho_{sample} = \frac{weig\,ht\ of\ sample\ \ (gram\,)}{volume\ \ pycnometer\ \ \ (ml\,)} \tag{3.4}$$

Figure 3.8: Gay-Lussac Pycnometer measurement

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 Preparation of waste cooking oil and FAME properties

In this sub chapter, the results from the WCO and FAME properties will be discussed. The feedstock pre-treatment required due to impurities in the waste WCO and water are mentioned.

The preparation results of WCO as a starting material for transesterification process was required for one step reaction, due to free fatty acid below 2% (Wang *et al*., 2006). Thus, the production of biodiesel was started with transesterification process without esterification process. The chemical and physical properties of WCO showed in Table 4.1.

Table 4.1: Chemical and physical properties of WCO.

| No | Parameter Analysis | Method | Unit | Value |
|---|---|---|---|---|
| 1 | Density at 40$^{o}$C | Pycnometer | kg/m$^{3}$ | 893.6 |
| 2 | Viscosity at 40$^{o}$C | Hydrometer | cm$^{2}$/s | 37.38 |
| 3 | Acid Value | Titrimetry | (mg KOH/g oil) | 2.21 |
| 4 | Free Fatty Acid as Palmitic | Calculation | % | 1.007 |
| 5 | Myristic Acid | GC | % | 3.27 |
| 6 | Palmitic Acid | GC | % | 35.31 |
| 7 | Stearic Acid | GC | % | 7.22 |
| 8 | Oleic Acid | GC | % | 21.06 |
| 9 | Linoleic Acid | GC | % | 17.20 |
| 10 | Linolenic Acid | GC | % | 15.50 |

The results of chemical and physical analysis of biodiesel from WCO using ultrasonic tubular reactor are shown in Table 4.2. All produced samples fulfilled the European standard limit in terms of acid value, kinematic viscosity, density, flash point, free glycerin, triglyceride, diglyceride, monoglyceride and methyl ester content. These results suggested that ultrasonic tubular reactors are the highest effective method for the production of quality biodiesel from WCO.

Table 4.2: Chemical and physical properties of biodiesel from WCO using ultrasonic tubular reactor.

| Parameters | WCO Biodiesel | Biodiesel Standard (EN 14214 and ASTM D6751) |
|---|---|---|
| Density at 40$^{o}$C (kg/m$^{3}$) | 853.1 | - |
| Kinematic Viscosity at 40$^{o}$C(cm$^{2}$/s) | 3.90 | 3.5 – 5.0 |
| Acid Value (mg KOH/g oil) | 0.067 | <0.5 |
| Flash Point ($^{o}$C) | 150 | >120 |
| Methyl Ester Contents (%wt) | 96.54 | >96.5 |
| Methanol Contents (%wt) | 0.0006 | <0.2 |
| Free Glycerol (%wt) | - | <0.020 |
| Triglycerides (%wt) | - | <0.2 |
| Diglycerides (%wt) | 0.0101 | <0.2 |
| Monoglycerides (%wt) | 0.1016 | <0.8 |

## 4.2 Preliminary analysis of FAME using ATR-IR

ATR-IR analysis was conducted for the preliminary analysis to observe the formation of desired functional group. In this case, the formation of metoxycarbonyl group substituting carbonyl group in the oil. Figure 4.1 is the spectrum of the starting material, namely crude waste cooking oil (CWCO), and the product of FAME was formed as WCO1, WCO2, WCO3, and WCO4. The absorption at 1099.4 cm$^{-1}$ peak showing the occurrence of -C–$CH_2$–$O^-$ group (alkoxide ion) in the CWCO spectra. Meanwhile the FAME product in WCO1, WCO2, WCO3, WCO4, the absorption was decreased and showed a new absorption at 1437.3 cm$^{-1}$ and 1197.3 cm$^{-1}$ peak, indicating a –$CH_3$ and O-$CH_3$ group has been formed. The most important characteristic peak is that of the O–$CH_3$ (1197.3 cm$^{-1}$) indicating the methyl formation of functional group of methyl and the occurrence of

transesterification process. Methyl functional group is an indicator of this reaction and the transesterification process has been successful and FAME was produced.

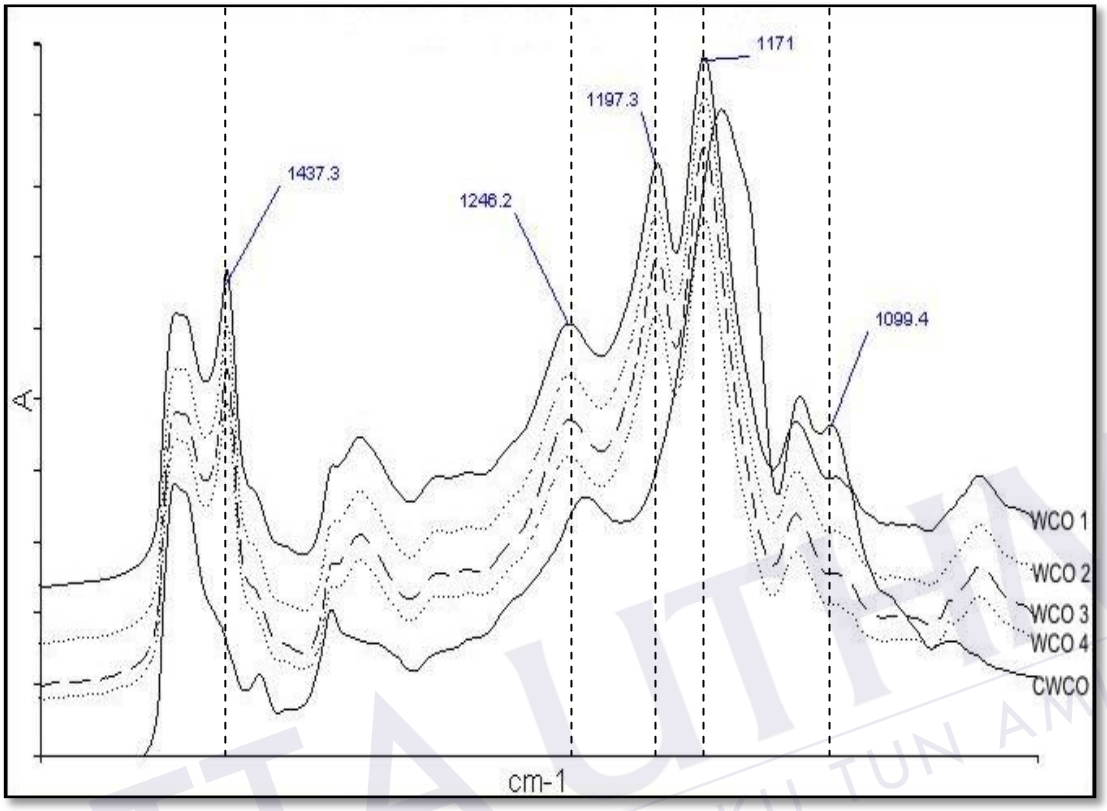



Figure 4.1: ATR-IR analysis of CWCO (crude waste cooking oil), WCO1 (1:9, 10 minute), WCO2 (1:6, 5 minute), WCO3 (1:9, 5 minute) and WCO4 (1:12, 5 minute)

## 4.3 WCO conversion to FAME using ultrasonic tubular reactor based on acid value

This sub chapter described the WCO conversion to FAME using ultrasonic tubular reactor based on acid value. The conversions of FAME were analyzed with acid value (as palmitic acid) according to AOCS Official Method Ca 5a-40 and was calculated from the mean of acid value (Av) of the oil layer by the following equation 4.1 (Wang *et al*., 2006).

$$Conversion\ (\%) = \left[1 - \frac{Av\ oil}{Av\ wco}\right] x\ 100 \qquad (4.1)$$

where, Oil and WCO refers to FAME layer and waste cooking oil, respectively.

### 4.3.1 Effect of reaction time on WCO conversion using ultrasonic technique

Figure 4.2 show the relationship between conversions of WCO to FAME products with reaction time. It is observed that as the reaction time increases, the concentration of TG decreased from the starting point. At reaction time of 3 minutes, the concentration of TG was found to be 0% and stable at 10 to 15 minute. This indicated that transesterification has occurred, which WCO was converted to FAME. The FAME produced drastically during the first 3 minute conversion about 64.11%. The following 5 – 15 minutes, conversion of FAME increased and constant until end.

The phenomena reaction under ultrasonic can be explained as follows; formation of cavitation bubbles could be stimulated by ultrasonic with sufficient energy. The symmetric collapse of the cavitation bubbles disrupts the phase boundary to create micro jets. As a result, oil and methanol form microscale fine emulsions, and they easily suspend each other (Thanh *et al*., 2010). At this point it was observed that FAME product was successfully produced and equilibrium can be reached in short reaction. The reaction time of 5 minutes, with molar ratio methanol to WCO is 6:1, with ultrasonic frequency of 20 kHz and catalyst NaOH of 1%wt was revealed high conversion of FAME up to 95.69%wt.

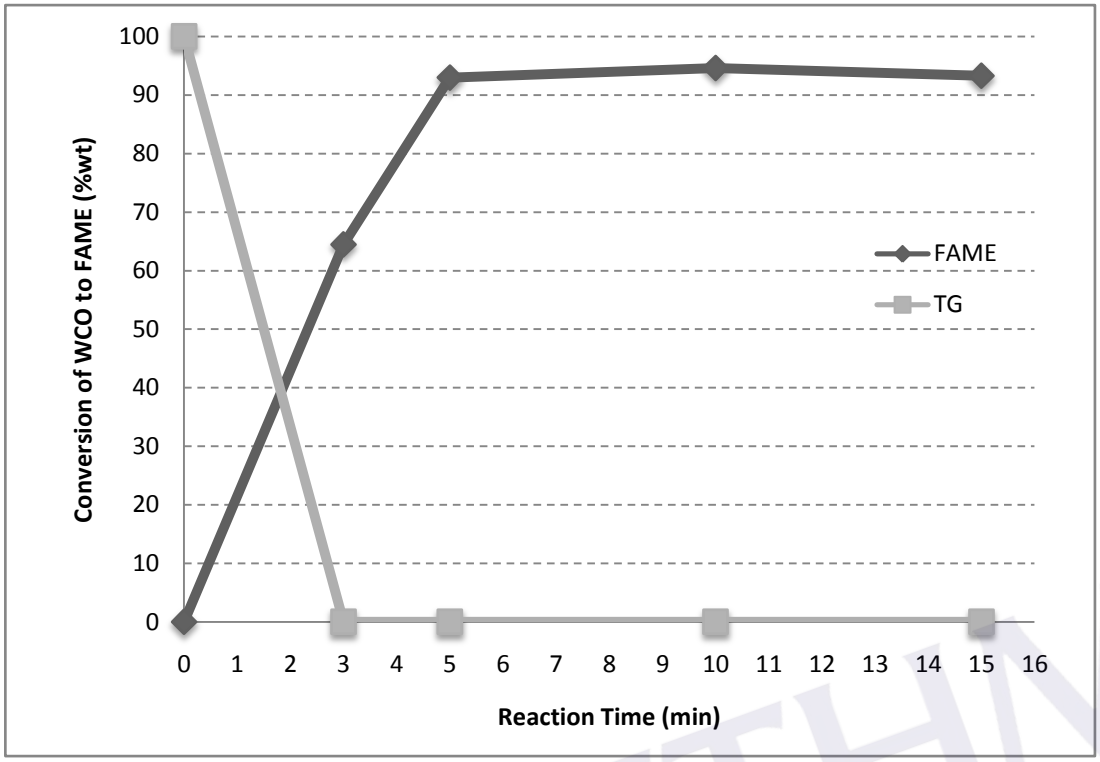



Figure 4.2: Reaction profile between reaction time and conversion at molar ratio of WCO to methanol (1:6), NaOH 1%wt, ultrasonic output power and frequency ultrasonic of 650 Watt and 20 kHz, respectively.

### 4.3.2 Effect of mole of methanol on WCO conversion using ultrasonic technique

Molar ratio of methanol to TG is one of the parameter important in determining of FAME. Experiment were conducted with molar ratio of methanol to TG ranging from 6:1, 9:1, 12:1 or 1.36, 2.03, 2.71 at methanol mole, respectively. The transesterification reaction stoichiometry requires three moles of alcohol per mole of triglyceride to yield three moles of FAME and one mole of glycerin (Wang *et al*, 2009). Referring to Figure 4.3, it was observed that with an increase in the molar ratio from 1.36 to 2.71, the conversion of WCO to FAME decreased slightly from 95.69%wt to 71.85%wt. The conversion of WCO increased rapidly at 1.36 moles at 5 minutes. Hanh *et al*, (2007) explained that the smaller emulsion droplets will result in increased contact surface area between the immiscible phases, resulting in higher rate of transesterification reaction. Its mean ultrasonic tubular reactor of a liquid with two phases is very effective to produce emulsion with small droplet size. In

contrast, the droplet size of the emulsion is larger when there is a large amount of methanol, and this result in a slower reaction at the initial stage (Thanh *et al.*, 2010).

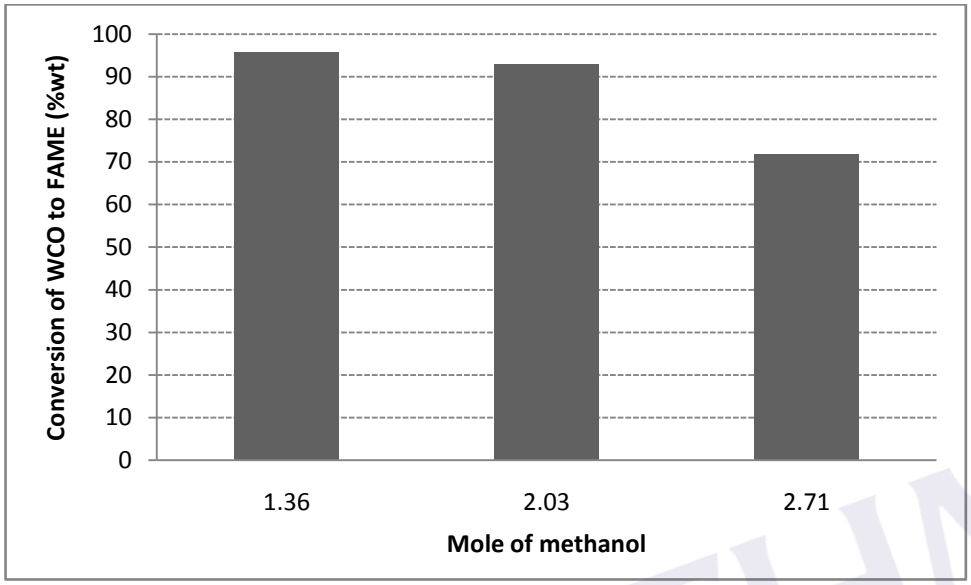



Figure 4.3: Effect of mole of methanol on the conversion of WCO to FAME at amount of catalyst 1 %wt, time reaction of 5 minute, ultrasonic output power and frequency ultrasonic 650 Watt and 20 kHz, respectively.

### 4.3.3 Effect of molar ratio on TG, DG and MG using ultrasonic technique

The step reaction transesterification mechanism which DG is the first intermediate and expected their accumulation in some extend. Figure 4.4 showed the amount of DG was low in WCO4 (biodiesel 4) and increased systematically at WCO3 (biodiesel 3), WCO2 (biodiesel 2), and biodiesel by mechanical stirring. The calculation of concentration of TG, DG and MG are shown in Appendix B. At WCO4 by ultrasonic method which the reaction of DG with ratio methanol of 12:1 is fast enough toward FAME product or almost completely converted to FAME. As compared to mechanical stirring for transeseterification process, the amount of DG is high due to the reaction was slower than ultrasonic technique.

During transesterification the amount of MG was high than of the DG. Sample WCO4 with molar ratio methanol to TG (12:1) was lower than WCO3, WCO2 and mechanical stirring. The tendency of molar ratio of methanol to TG against DG and MG were decreased with increased molar ratio methanol to TG.

Transesterification reaction with vigorously agitated by the ultrasonic jet obtained the movement of reactant droplets in the emulsion (Thanh *et al*., 2010). This shows, DG on the surface of the droplets promptly reacts with methanol to release MG and FAME, and then MG was immediately consumed by methanol to form glycerol. Compared with mechanical stirring, the concentration of DG and MG showed higher over than ultrasonic process.

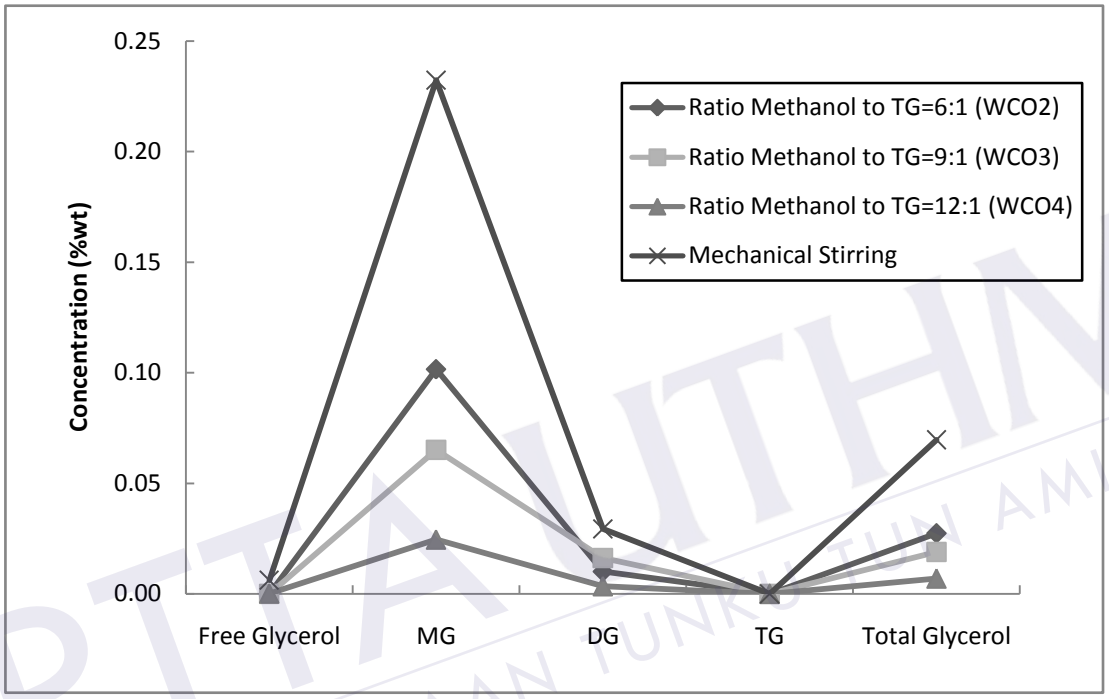



Figure 4.4: Correlation between Concentrations (%wt) TG, MG, DG, Total and Free Glycerol with molar ratio methanol to TG at ultrasonic output power and frequency at 650 Watt and 20 kHz, respectively with reaction time 5 minute and NaOH 1%wt.

## 4.4 Optimizations of biodiesel process using ultrasonic tubular reactor on ester contents

### 4.4.1 Effect of WCO to Methanol molar ratio

At first, the effect of WCO to Methanol (MeOH) molar ratio on the ester contents is investigated to understand the optimum condition using ultrasonic technique. Figure 4.5 is showed the changes in the ester contents at various molar ratios of WCO to MeOH with NaOH catalyst of 1%wt under ultrasonic tubular reactor. The optimum

ester contents were observed of 96.54%wt, 85.24%wt, 92.55%wt at 5 minutes for molar ratio (WCO to MeOH) of 1:6, 1:9 and 1:12, respectively. It was indicated that the ultrasonic frequency form a fine emulsion at 5 minute, due to the interface area between MeOH to oil was increased, it caused the rate of the transesterification can be enhanced, and reduce the amount of excess MeOH required. On the other hand, the ester contents at molar ratio 1:6, 1:9, 1:12 were decreased at 10 to 15 minutes. The reaction of transesterification is reversible. It was indicated that the reaction reverse toward to TG due to the equilibrium reaction occurred in 5 minutes.

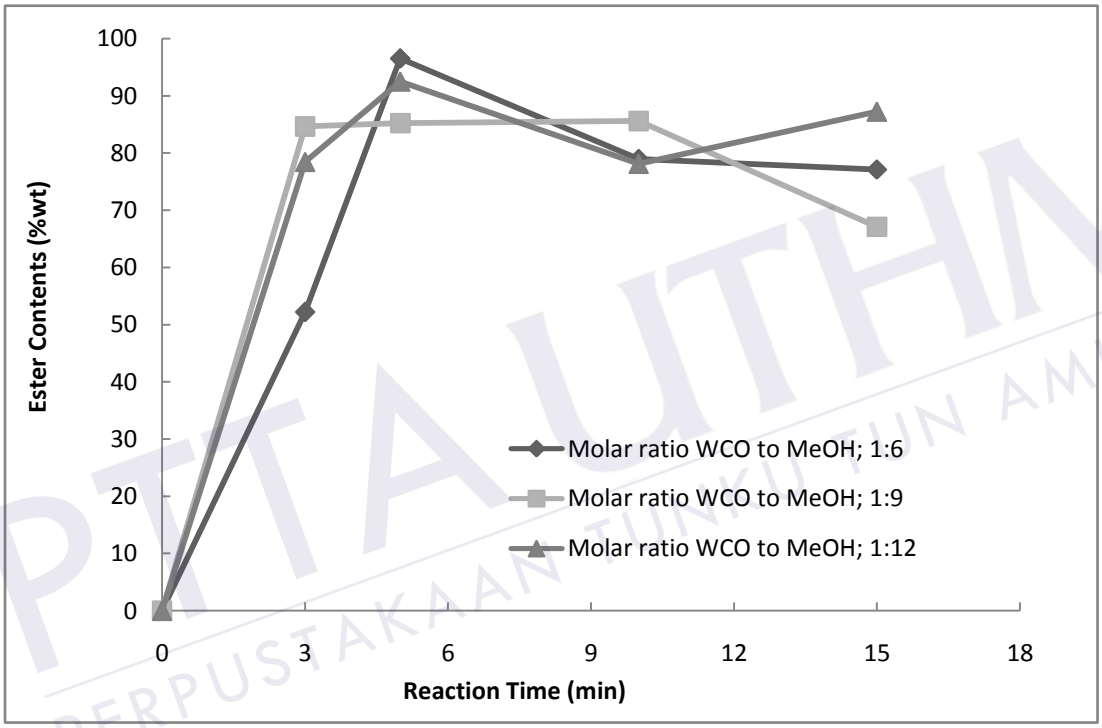



Figure 4.5: Effect of molar ratio of methanol to WCO on ester contents (%wt) at NaOH concentration of 1 %wt, ultrasonic output power and frequency of 650 Watt and 20 kHz, respectively.

### 4.4.2 Effect of catalyst amount

Figure 4.6 showed the effect of ester contents and reaction time with various amount of catalyst under ultrasonic tubular reactor. The maximum ester contents were observed at about 1%wt of NaOH catalyst in molar ratio WCO to MeOH of 1:6 at 5 minute reaction time. In this case, the ester contents on various amount of catalyst

were the same when increased at 3 to 5 minutes of reaction time and decreased at 5 to 15 minutes of reaction time. Excess catalyst reacted with the WCO, leading to the formation of soap, thus as the catalyst concentration increased, the separation of esters become more difficult. A minimal amount of 0.5%wt to 0.75%wt NaOH catalyst was adequate in propelling the transesterification reaction using ultrasonic tubular reactor, however an amount of 1% wt gave the best yields. As shown in the figure, high amount of NaOH catalyst (1.25%wt) form soaps in the presence of large residues of fatty acids resulting in emulsion formation between soaps and water molecules, thus leading to low yields of ester contents.

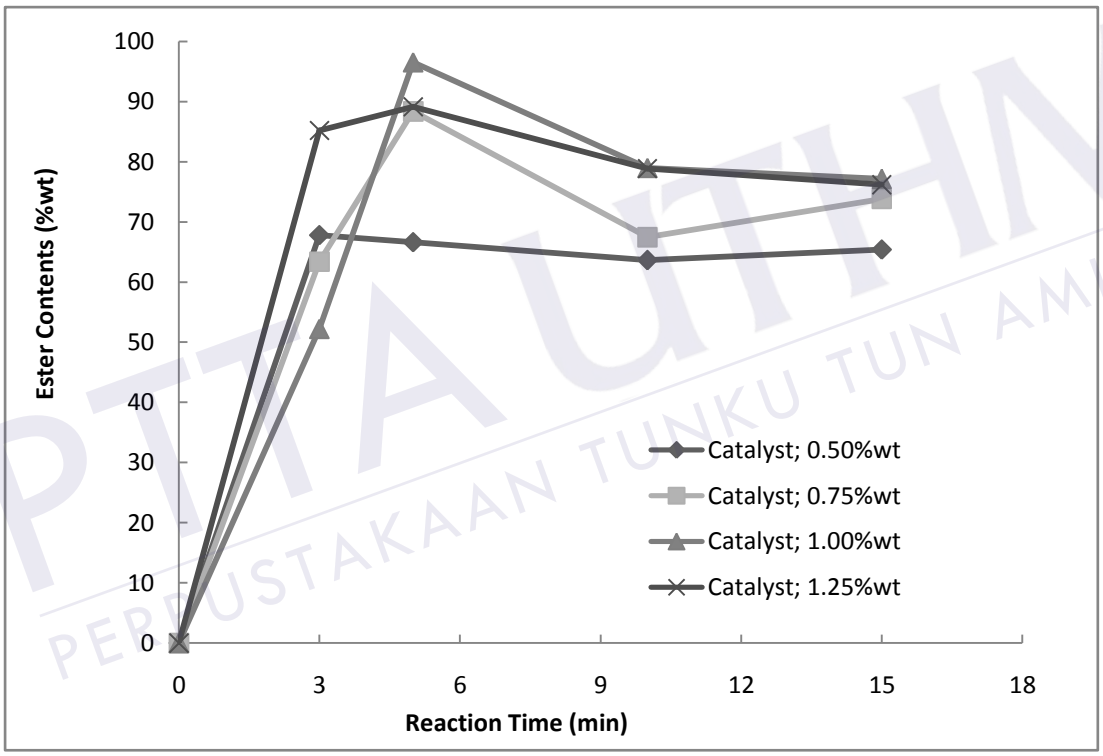



Figure 4.6: Effect of amount of NaOH catalysts on ester contents (%wt) at molar ratio methanol to WCO of 6:1, ultrasonic output power and frequency of 650 Watt and 20 kHz, respectively.

### 4.4.3 Effect of ultrasonic frequency

This step was to establish the influence of ultrasonic frequency on the ester contents. From the obtained results in Figure 4.7, the reactions performed under ultrasonic at 20 kHz produced higher ester contents than 18 and 22 kHz in 5 minutes reaction.

Usually there are no important differences in the formation of the cavitation bubbles at 18 and 22 kHz, but in this case, at 20 kHz the reaction time was shorter to raise the equilibrium reaction. After less than 3 minutes of sonication, the mixture form emulsification. This is due to collapse of the cavitation bubbles and ultrasonic jets that impinge WCO to MeOH, disrupting the phase boundary and causing emulsification (Hanh *et al.*, 2008). On the other hand, At 5 minutes when the frequency ultrasonic increased from 20 to 22 kHz, the emulsion was formed in a higher amount and some ester is trapped into emulsion, causing the ester contents to decrease. At higher frequencies, the collapses of cavitation bubbles are not strong enough to impinge one liquid to the other (Stavarache *et al*., 2005). The mixing between the two immiscible layers (MeOH and WCO) is very poor hence emulsification does not occur, and the transesterification takes place mainly at the boundary between the two layers.

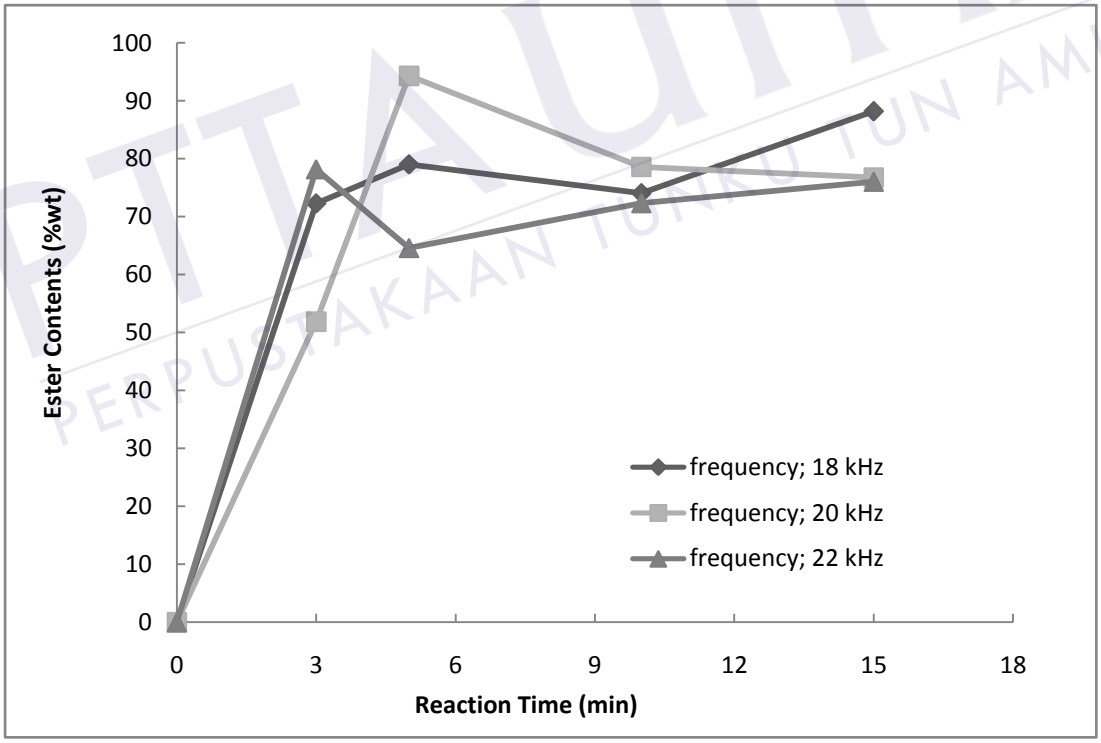



Figure 4.7: Effect of ultrasonic frequency on ester contents (%wt) at molar ratio WCO to MeOH of 1:6, amount of NaOH catalyst of 1% and ultrasonic output power of 650 W.

### 4.4.4 Effect of ultrasonic output power

The optimal parameters such as WCO to MeOH molar ratio (1:6), NaOH catalyst (1%wt), ultrasonic frequency (20 kHz) were kept constant and the ultrasonic output power was varied from 325 W to 975 W for the same operating volume of the reaction mixture. The result is presented in Figure 4.8. At output power of 325 Watt, the ester contents were around 75.20%wt at 5 minutes of reaction but when the output power was increased to 650 Watt, the ester contents also increases to about 96.54%wt. This can be explained, the ultrasonic output power (intensities) provoke larger amplitude at the vibrating surface in contact with the liquid (Hoffmann *et al.*, 1999). On the other hand, increases in the ultrasonic output power from 650 Watt to 975 Watt at 5 minutes, the ester contents were decreased. This can be attributed to the fact that at higher output power ultrasonic usually creates more and larger bubbles, which may coalesce and lead to less transient events. But according to Hingu, Gogate & Rathod, (2010) higher power level ultrasonic will decrease transfer of energy into the system and hence lower cavitational activities.

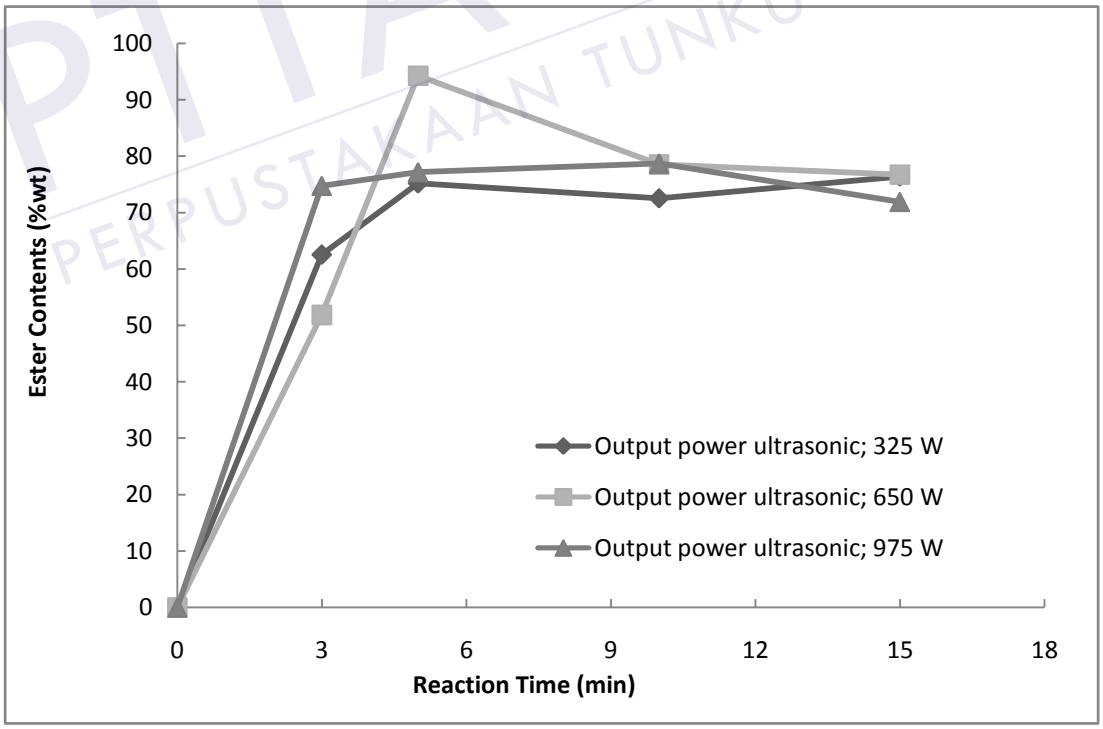



Figure 4.8: Effect of ultrasonic output power on ester contents (%wt) at molar ratio WCO to MeOH of 1:6, amount of NaOH catalyst of 1% and ultrasonic frequency of 20 kHz.

### 4.4.5 Comparison of ultrasonic technique with mechanical stirring to synthesis biodiesel based on acid value calculation

The results of optimization using ultrasonic tubular reactors were compared with the conventional ultrasonic cleaner and also mechanical stirring method as shown in Figure 4.9. Conventional ultrasonic cleaner and mechanical stirring experiments were performed using the same amounts of reactants and molar ratio WCO to MeOH used in the ultrasonic tubular reactor. The calculation of conversion WCO to FAME followed the equation 4.1.

The ultrasonic tubular reactor and cleaner were obtained 98.39%wt and 30.06%wt of conversion from WCO to FAME at 5 minutes, respectively. Whereas the mechanical stirring method revealed much lower conversion of 6.08%wt over similar operation time at 5 min. This indicated that the reaction of transesterification using ultrasonic tubular reactor is quicker to form biodiesel compared to mechanical stirring approach. Because the ultrasonic technique is generated wide range of cavitation bubble sizes and a greater density of cavitation bubbles. This provides faster and better cleaning, faster sonochemical reactions, faster physical reactions, and faster liquid degassing (Prokic, 2001). But ultrasonic (tubular reactor and cleaner) gave high ester contents compared to mechanical stirring.

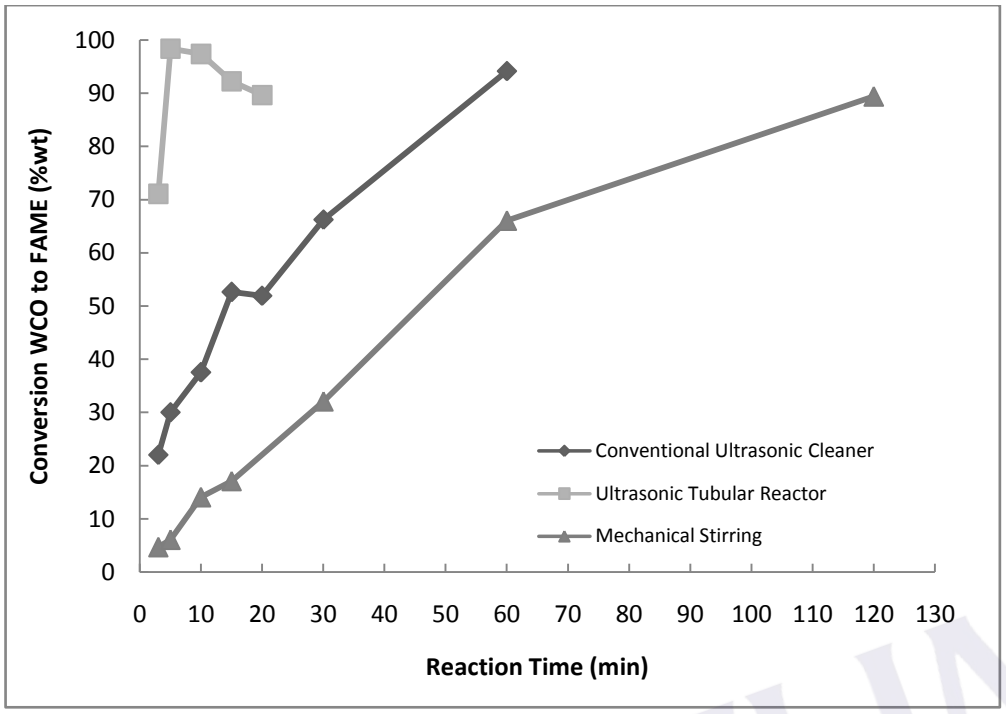



Figure 4.9: Comparison of ultrasonic and mechanical stirring method on conversion of WCO to FAME. Reaction conditions: WCO to MeOH ratio of 1:6 and NaOH amount 1 %wt; Ultrasonic tubular reactor: frequency 20 kHz, with output power 650 Watt in close system. Conventional ultrasonic cleaner: frequency 35 kHz with input power 140 Watt in open system. Mechanical Stirring: stirrer speed 350 rpm in open system.

## 4.5 Liquid-liquid equilibrium (LLE) of WCO-FAME-Methanol

In order to fully understand the transesterification reaction path within the ultrasonic tubular reactor, the composition path was characterized with the ternary phase diagram of WCO–FAME–Methanol (MeOH). The figure explaining the solubility of three compounds and the curve of LLE is area to occur the reaction. Eleven reactions were carried out by varying the WCO to methanol ratio (1:6, 1:9 and 1:12), catalyst concentration (0.5, 0.75, 1 and 1.25%wt of WCO) and frequency ultrasonic (18, 20, and 22 kHz)

### 4.5.1 Phase equilibrium of WCO-FAME-Methanol on molar ratio WCO to methanol

Figure 4.10 shows the effect of WCO to MeOH molar ratio on the composition path during the WCO biodiesel using 1 wt. % NaOH catalyst, frequency ultrasonic of 20 kHz, output power ultrasonic of 260 Watt and 3-15 minute reaction time. WCO and methanol are not mutually soluble so that the initial reaction composition all starts from the right line of MeOH–WCO, regardless of the initial MeOH to WCO molar ratio. However, with the increase of FAME ratio during the transesterification, the methanol to WCO ratio shows significant effect on the time for the reaction composition entering into the homogenous phase of the ternary system of WCO–FAME–MeOH. If the starting mixture at 1% wt NaOH catalyst has a molar ratio of 1:6 (open square), only 3 min are required for the reaction to be homogenous. After 3 min, the FAME was rapidly occurred with molar ratio 1:6, 1:9 and 1:12. This phenomenon revealed the ultrasonic is faster in converting WCO to FAME.

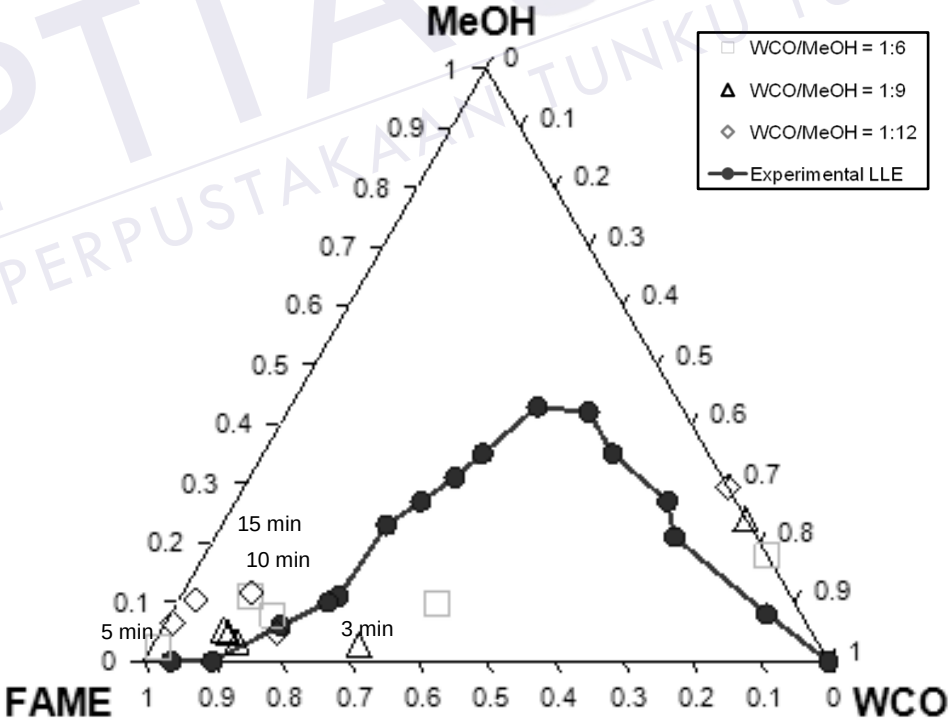



Figure 4.10: Effect of WCO to MeOH molar ratio on the ternary composition paths of WCO biodiesel using ultrasonic tubular reactor

### 4.5.2 Phase equilibrium of WCO-FAME-Methanol on amount of NaOH catalyst

Similar with that shown in Figure 4.10, all reaction paths are similar as shown in Figure 4.11, as the experiments are performed at 0.5, 0.75, 1 and 1.25 %wt of NaOH at the constant molar ratio of 1:6 and frequency ultrasonic of 20 kHz. However, the time for the reaction to reach a steady state reduces with the increase of catalyst concentration whereas the final equilibrium concentration of each component remains almost the same. For the catalyst concentrations of 0.5, 0.75,1 and 1.25%wt, it takes 5 min for the system to be homogeneous as shown on the reaction path line in Figure 4.11, and it will take 5, 10 and 15 min to achieve almost the same final equilibrium FAME concentration, respectively.

The main factor for LLE in this system is solubility. The experimental data showed the increase value of solubility with the number of double-carbon bond due to the polarity of this group. On the other side, solubility increases with the reducing of fatty acids molecular weight. The phenomenon was clearly shown after 3 min which the FAME was formed.

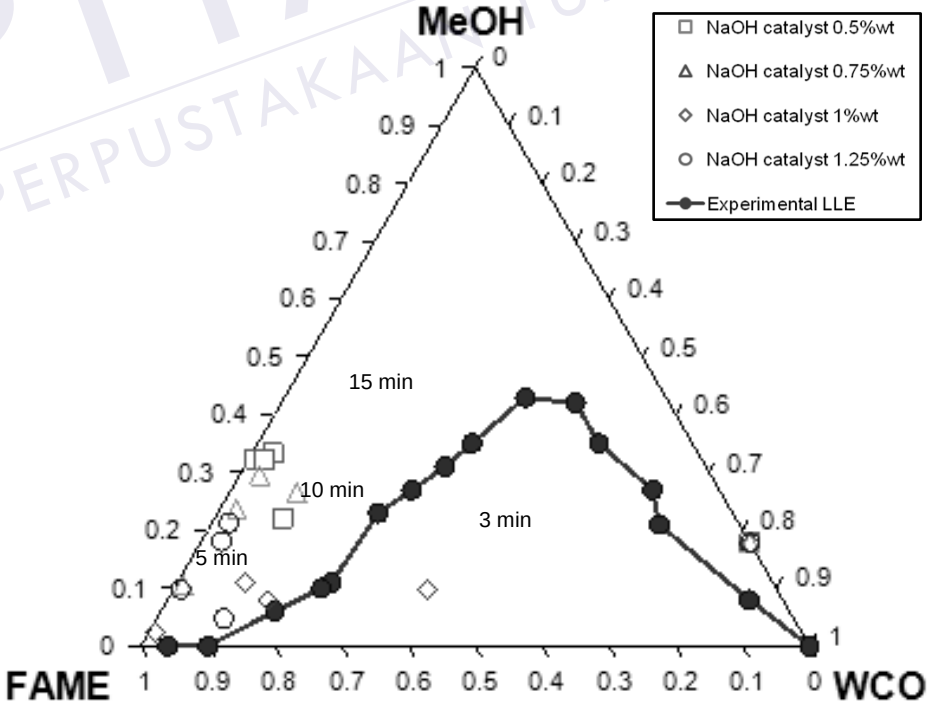



Figure 4.11: Effect amount of catalyst on the ternary composition paths of WCO biodiesel using ultrasonic tubular reactor.

### 4.5.3 Phase equilibrium of WCO-FAME-Methanol on ultrasonic frequency

The reaction was studied at different ultrasonic frequency in the phase of equilibrium WCO-FAME-Methanol (MeOH) as showed on Figure 4.12. This experiment carried out under ultrasonic tubular reactor at different frequency. The same tendency is observed in the case of frequency at 18, 20, and 22 kHz. At 3 minute reaction, all the variety of frequency ultrasonic was formed to biodiesel. The cavitation from wave of ultrasonic was given vigorous mixing and it can be occurred the two phase (biodiesel and glycerol layer). The variety of frequencies ultrasonic not effect on the solubility.

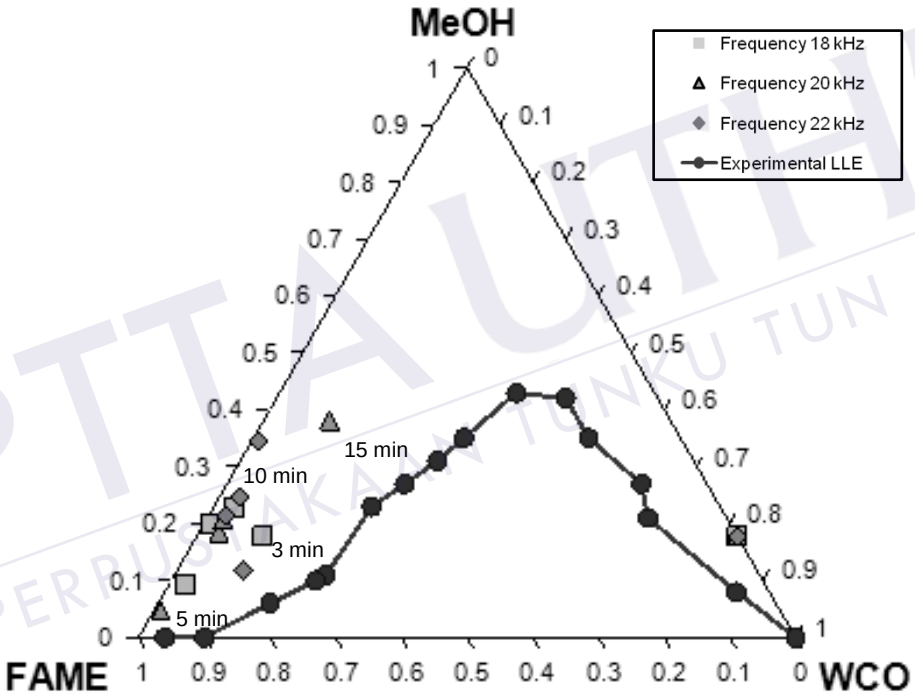



Figure 4.12: Effect of frequency ultrasonic on the ternary composition paths of WCO biodiesel using ultrasonic tubular reactor.

## 4.6 Semi continuous of ultrasonic tubular reactor

In the case of a semi continuous ultrasonic tubular reactor, the length of time the reagents remain in the reactor was translates into the residence time. The results of

semi continuous run for biodiesel from WCO carried out in the small size reactor ultrasonic tubular under these conditions are presented in Figure 4.13.

The optimum process in ultrasonic tubular reactor batch scale was used to performed semi continuous ultrasonic tubular reactor. About 15 kg of WCO, 20 kHz of frequency, and 260 Watt of output ultrasonic, 5.56 ml /s of flow rate WCO as starting material and molar ratio of WCO to MeOH (1:6) were conducted the semi continuous of ultrasonic tubular reactor. The result of biodiesel produce from WCO is shown in Table 4.3.

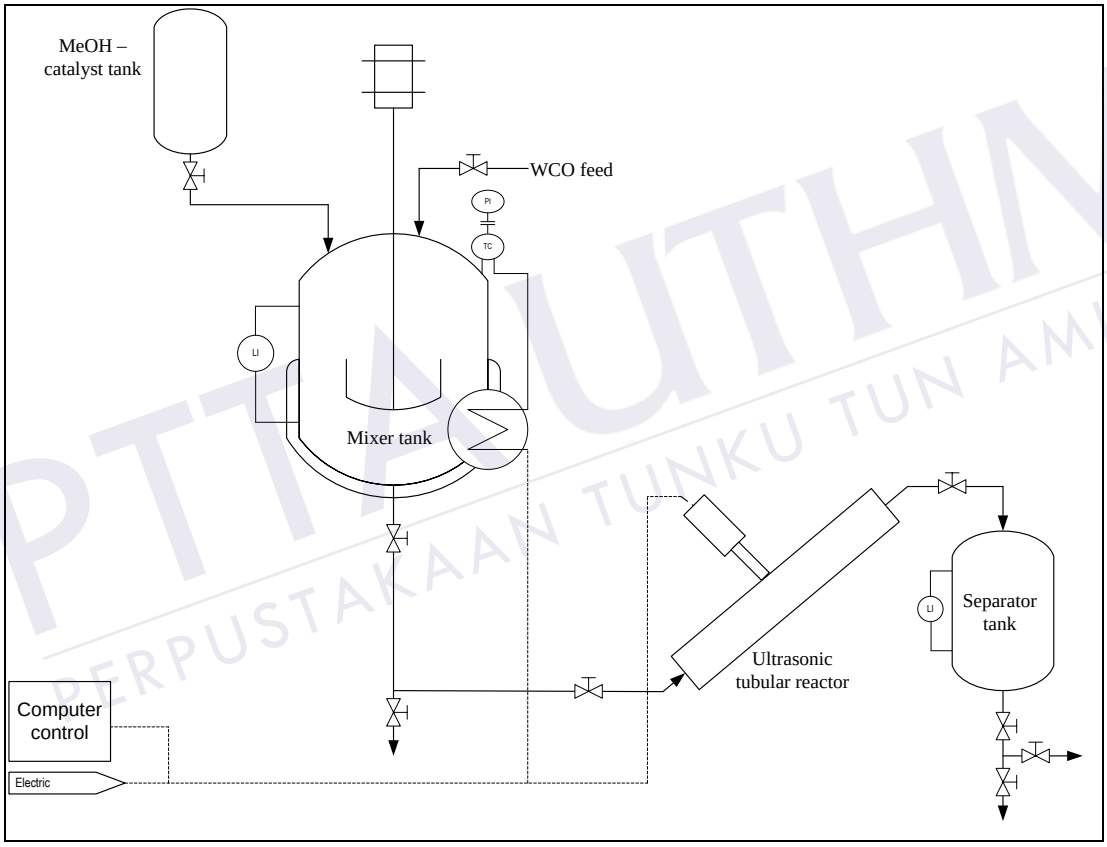



Figure 4.13: Schematic of semi continuous ultrasonic tubular reactor for biodiesel process from WCO.

Table 4.3 shows the results of chemical and physical properties for biodiesel based on WCO using semi continuous of ultrasonic tubular reactor. The result was fulfill the biodiesel standard (EN 14214 and ASTM D6751) for viscosity, density, flash point, acid value and FFA.

Table 4.3: Chemical and physical properties of WCO biodiesel using semi continuous ultrasonic tubular reactor.

| Parameter | WCO Biodiesel | Biodiesel Standard (EN 14214 and ASTM D6751) |
|---|---|---|
| Viscosity at 40$^{o}$C (mm$^{2}$/s) | 3.9 | 3.5 - 5.0 |
| Density (g/ml) at 20$^{o}$C | 0.820 | 0.860 - 0.900 (at 15 $^{o}$C) |
| Flash Point ($^{o}$C) | 138 | > 120 |
| Acid Value (mg KOH/g oil) | 0.70 | < 0.8 |
| FFA (%) | 0.35 | - |
| Conversion Base Acid Value (%wt) | 98.39 | - |

# CHAPTER 5

# DISSEMINATION OF BIODIESEL PROCESS

## 5.1 Introduction

The office for research management innovation commercialization and consultancy (PPI)- Universiti Tun Hussein Onn Malaysia (UTHM) has a program for transfer knowledge to community and society in Batu Pahat. Many small industries have been consultancy and cooperation with UTHM for innovation, incubator product and so on. One of small industry has interesting to develop the renewable energy. It is Azhar Food, Sdn Bhd which it is one of the grown companies (family business) which have the product focus on a snack or prawn crackers, such as tapioca chips and other crackers. The company still has several technical problems regard to efficiency of the energy, waste cooking oil (WCO) and waste water treatment. The several potential problems solving in optimizing the recycle loop (environmental friendly) are the usage of cooking oil as the potential raw material for biodiesel. In this company approximately 400 kg of used oil is collected every week. Biodiesel is one of alternative solution to solve the problem and also to increase the added value of WCO.

On the other hand, this idea was purposed to proposal of Knowledge Transfer Program (KTP) and it was approved by Kementerian Pengajian Tinggi Malaysia (No letter: Ruj: ktp/bil6-37/11).

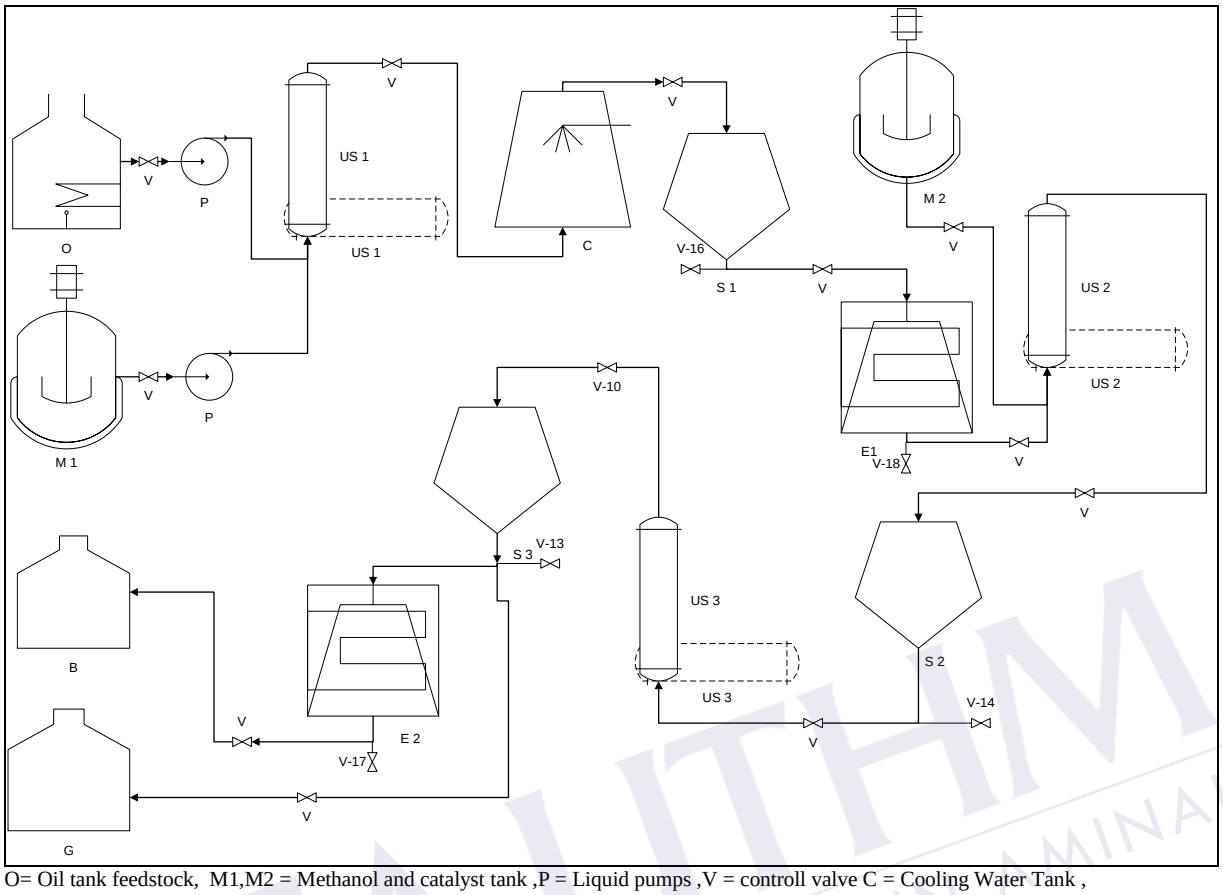
There are many existing technologies to make biodiesel, the selection of method for this research was described section 5.2.

## 5.2 Selection method

### 5.2.1 Analysis of design pilot plant by ultrasonic system

The concept and design of ultrasonic reactor for biodiesel process is continuous system including 3 processes (esterification, transesterification and washing process). The main equipment in this system equipped 2 stirring reactor, 3 ultrasonic tubular reactors, 3 separators and 2 evaporators. The advantages of this system are continuous system and also the reaction time is shortened. Meanwhile, the investment for this system is very expensive due to the technology ultrasonic for pilot plant scale need high cost. However, the end user in this research is small industry and also community industry in Batu Pahat. Therefore, the transfer technology to industry must be innovative and also very simple.

Figure 5.1 showed the concept and design process for biodiesel production by ultrasonic technique which the figure adoption in Prototype Development Research Grant scheme 2011 (PRGS). The influence of condition and parameter in this system was determined in the subchapter 4.6 for semi continuous ultrasonic system.




O= Oil tank feedstock, M1,M2 = Methanol and catalyst tank ,P = Liquid pumps ,V = controll valve C = Cooling Water Tank , E1,E2 = Evaporator, US1,US2,US3 = Ultrasonic reactor , S1,S2,S3 = Separator tank ,B= Biodiesel product tank ,G = Glycerol tank.

Figure. 5.1 Schema design of continuous ultrasonic tubular reactor for biodiesel process at pilot plant scale. (Sebayang, 2011)

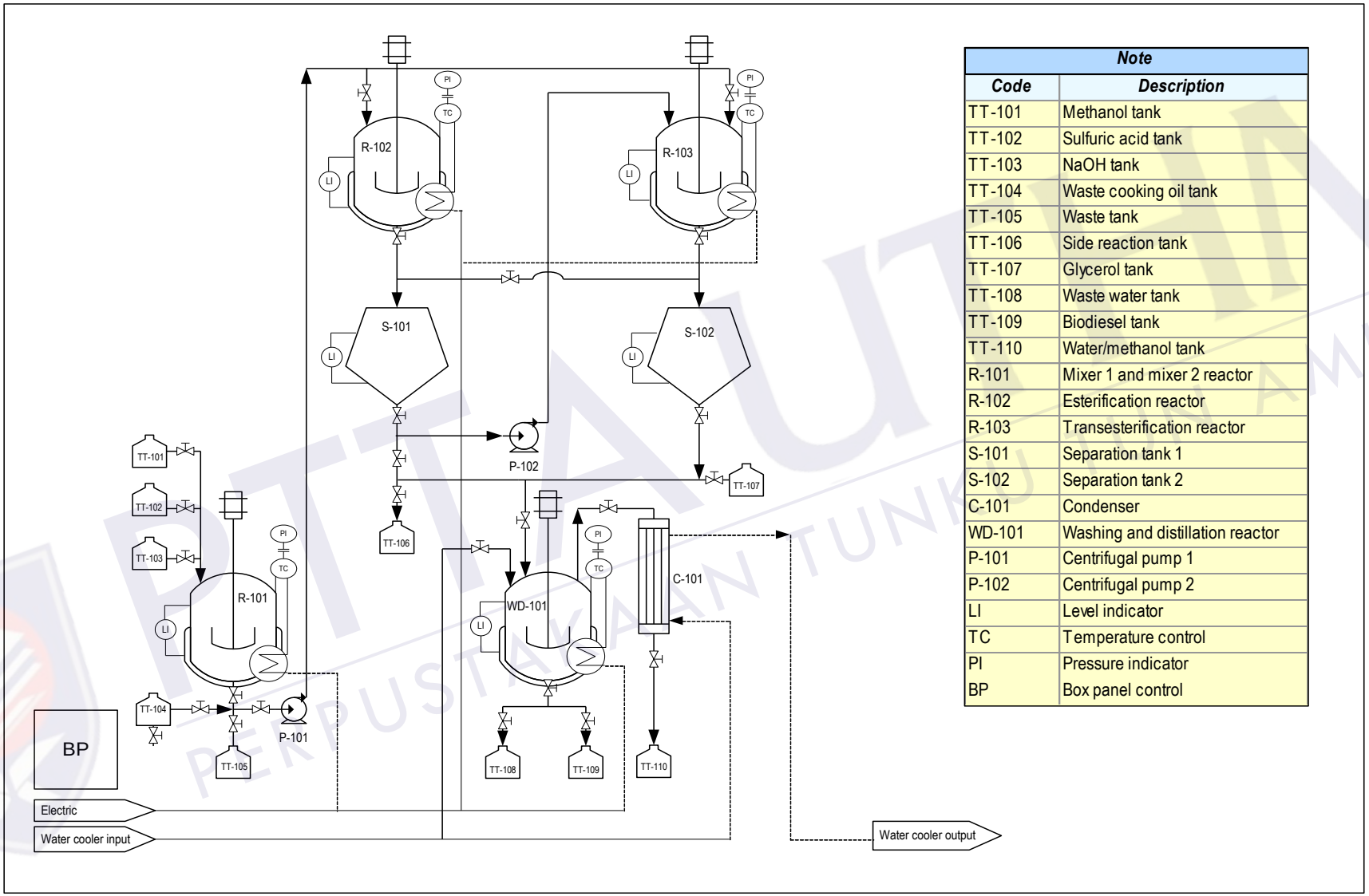
### 5.2.2 Analysis of design pilot plant by mechanical stirring method

The mechanical stirring method is one of conventional technique for making biodiesel fuel. Design pilot plant by mechanical stirring in this research is shown in Figure 5.2. The concept and design process was described in the below. However, the mechanical stirring method has a benefit compare to ultrasonic technique such as simple process, lower cost of equipment, and so on. The comparison of their method is shown in Table 5.3.

#### 5.2.2.1 Technical description

A conceptual biodiesel process flow diagram is shown in Figure 5.2. The design of process biodiesel from WCO used two step reactions (esterification and transesterification process). According results on sub chapter 4.4.5, the condition of transesterification reaction is used reaction temperature of 60 -70°C in 2 hours with catalyst concentration of 1% based on the mass of oil, and molar ratio of methanol to oil of 6:1. The conversion of WCO to biodiesel obtained at 98%wt. (based on sub chapter 4.4.5)

Methanol and sulfuric acid are mixed in the mixer 1 (R101) and the mixture WCO (TG and FFA) are transferred to esterification reactor (R102), after that the mixture Methanol-sulfuric acid mixed together in R102 with the mixture WCO and they heated to 60-70$^{o}$C for 2 hours. Upon completion, input the mixture from R102 to separator 1 (S101), which the TG-FFA is in upper layer and water-methanol-catalyst is in lower layer. The mixtures of TG-FFA are moved to transesterification (R103) and added with methanol-NaOH from mixer 2 (R101). The reaction is completed after 2 hours and the mixture is transferred into separator 2 (S102). The FAME mixture formed the upper layer and the glycerol form in the lower layer. Separate the FAME, and moved to washing reactor (WD101). In this process, added water to WD101 and mix the mixture FAME-water for 1 hour (until pH 6-7) and separate water from FAME. After that, evaporate the water from FAME mixture at 100$^{o}$C for 1 hour.




| Note | |
|---|---|
| **Code** | **Description** |
| TT-101 | Methanol tank |
| TT-102 | Sulfuric acid tank |
| TT-103 | NaOH tank |
| TT-104 | Waste cooking oil tank |
| TT-105 | Waste tank |
| TT-106 | Side reaction tank |
| TT-107 | Glycerol tank |
| TT-108 | Waste water tank |
| TT-109 | Biodiesel tank |
| TT-110 | Water/methanol tank |
| R-101 | Mixer 1 and mixer 2 reactor |
| R-102 | Esterification reactor |
| R-103 | Transesterification reactor |
| S-101 | Separation tank 1 |
| S-102 | Separation tank 2 |
| C-101 | Condenser |
| WD-101 | Washing and distillation reactor |
| P-101 | Centrifugal pump 1 |
| P-102 | Centrifugal pump 2 |
| LI | Level indicator |
| TC | Temperature control |
| PI | Pressure indicator |
| BP | Box panel control |

Figure 5.2: Design of biodiesel process from WCO at 100 kg WCO per batch.

#### 5.2.2.2 Mass balance

The mass balances for each compound have been derived for the individual unit operations per batch. The assumed and calculation of mass balances is shown in Appendix C. In order to achieve the required total weekly production of 606 kg biodiesel, an output of 101 kg/batch biodiesel and a total number 6 batches/week is defined.

Based on Figure 5.3 shown the material balance in stream 16 which it is defined WCO of flow rate at 101.024 kg/batch. The molar ratio methanol to WCO (6:1) is flow rate of 11.425 kg/batch (stream 3). According in the previous resulted (sub chapter 4.4.5), the catalyst concentration of sodium hydroxide (1% based on oil) needed 0.95 kg/batch (stream 11). The completed of mass balance shown in Table 5.1.

The choice of process design, the batch size in the pre-treatment/mixer reactor (R101) section is defined to be same of the batch size in the esterification and transesterification reaction section. This mass ratio ensures a continuous succession of the transesterification reactions, which ultimately results in a constant continuous flow into the purification section after the initial downtime required for processing the first batch of pre-treated WCO. Therefore, in the stream 5 as pre-treated WCO per batch accumulated in tank S101 and S102, is equivalent to two times stream 5, the amount of pre-treated WCO used for each batch in the transesterification reaction.

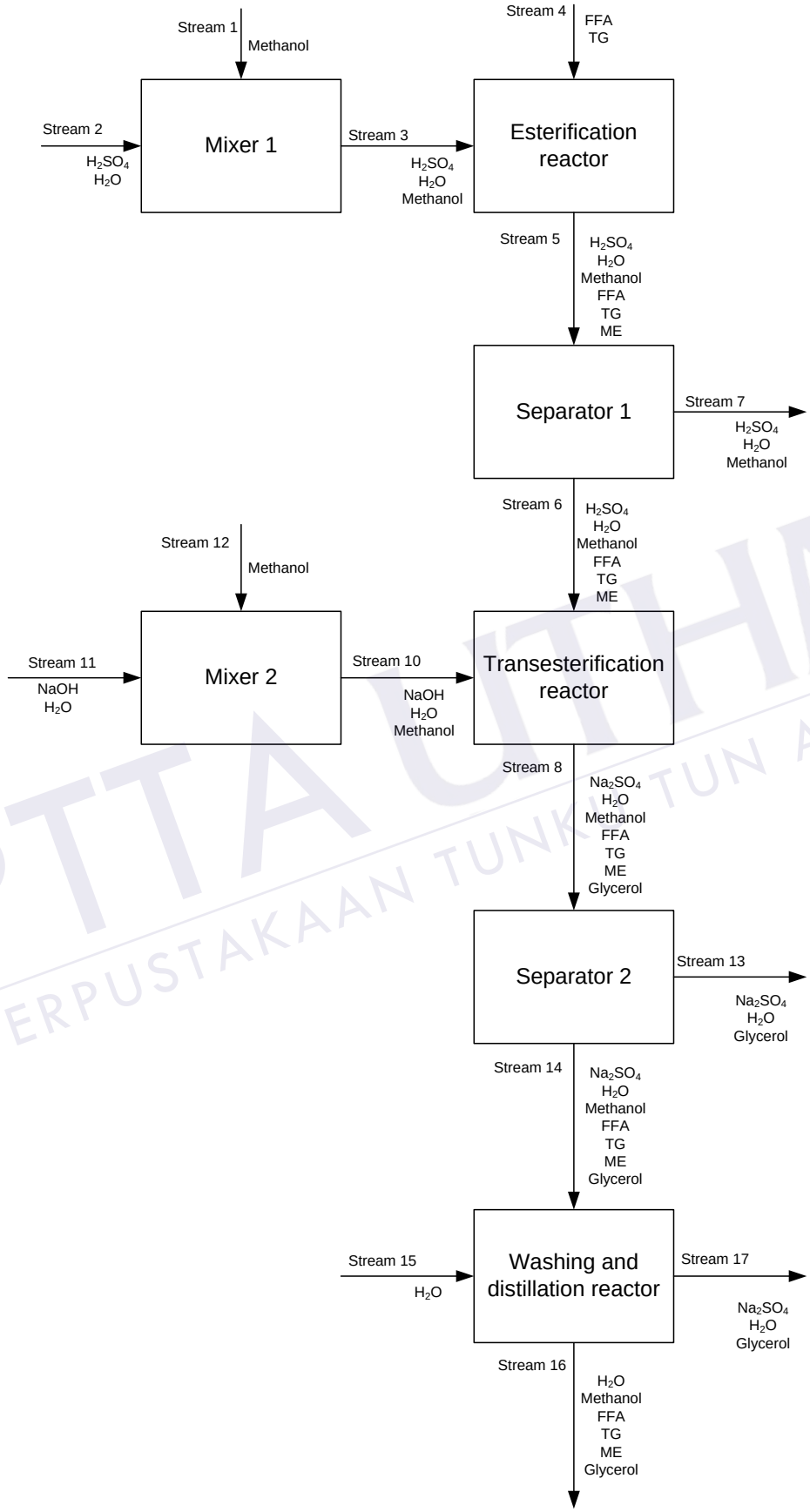



Figure 5.3: Schematic flow of diagram for biodiesel process

Table 5.1: Material balance of biodiesel process for 100 kg WCO per batch

| Compound | Stream (kg/batch) | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 |
| $H_2SO_4$ | | 0.0485 | 0.0485 | | 0.0485 | 0.0005 | 0.0480 | | | | | 0.0005 | | | | |
| $H_2O$ | 0.2332 | 0.0015 | 0.2347 | | 0.5641 | 0.0001 | 0.0313 | 0.4186 | 0.4186 | | 0.4186 | 0.4144 | 0.0002 | 29.6355 | 0.2964 | 29.3433 |
| MeOH | 11.4254 | | 11.4254 | | 10.8384 | 0.1084 | 10.7300 | 0.3196 | 20.5102 | | 20.5102 | | 0.3196 | | | |
| TG | | | | 95.0000 | 95.0000 | 95.0000 | | 1.8876 | | | | | 1.8876 | | 1.8876 | |
| FFA | | | | 5.0000 | 0.0539 | 0.0539 | | 0.0539 | | | | | 0.0539 | | 0.0539 | |
| ME | | | | | 5.1907 | 5.1907 | | 98.7851 | | | | | 98.7851 | | 98.7851 | |
| NaOH | | | | | | | | 0.9500 | 0.9500 | 0.9500 | | 0.9405 | 0.0095 | | | 0.0095 |
| Glycerol | | | | | | | | 9.9820 | | | | 9.8822 | 0.0998 | | 0.0010 | 0.0988 |
| $Na_2SO_4$ | | | | | | | | 0.0007 | | | | 0.0007 | 0.0000 | | | 0.0000 |
| Total | 11.6586 | 0.0500 | 11.7086 | 100.0000 | 111.6956 | 100.3536 | 10.8093 | 112.3975 | 21.8788 | 0.9500 | 20.9288 | 11.2383 | 101.1558 | 29.6355 | 101.0240 | 29.4516 |

| Compound | Stream (kmole/batch) | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 |
| $H_2SO_4$ | | 0.0005 | 0.0005 | | 0.0005 | 0.0000 | 0.0005 | | | | | | | | | |
| $H_2O$ | 0.0130 | 0.0001 | 0.0130 | | 0.0313 | 0.0000 | 0.0017 | 0.0233 | 0.0233 | | 0.0233 | 0.0230 | 0.0002 | 1.6464 | 0.0165 | 1.6302 |
| MeOH | 0.3570 | | 0.3570 | | 0.3387 | 0.0034 | 0.3353 | 0.0100 | 0.6410 | | 0.6410 | | 0.0100 | | 0.0100 | |
| TG | | | | 0.1107 | 0.1107 | 0.1107 | | 0.0022 | | | | | 0.0022 | | 0.0022 | |
| FFA | | | | 0.0185 | 0.0002 | 0.0002 | | 0.0002 | | | | | 0.0002 | | 0.0002 | |
| ME | | | | | 0.0183 | 0.0183 | | 0.3438 | | | | | 0.3438 | | 0.3438 | |
| NaOH | | | | | | | | 0.0237 | 0.0238 | 0.0238 | | 0.0235 | 0.0002 | | | 0.0002 |
| Glycerol | | | | | | | | 0.1085 | | | | 0.1074 | 0.0011 | | 0.0000 | 0.0011 |
| $Na_2SO_4$ | | | | | | | | 0.0000 | | | | 0.0000 | 0.0000 | | | 0.0000 |
| Total | 0.3700 | 0.0006 | 0.3705 | 0.1292 | 0.4997 | 0.1326 | 0.3375 | 0.5116 | 0.6880 | 0.0238 | 0.6642 | 0.1539 | 0.3577 | 1.6464 | 0.3727 | 1.6315 |

#### 5.2.2.3 Equipment design and specifications

There are 6 main pieces of equipment in the biodiesel production plant: 3 reactors, 2 separators and 1 multi function reactor (washing and distillation process). In designing the reactor for this process, the volumes were first determined using the mass balance. The volumes of all of the components entering the reactor were added together to give the total liquid volume of the reactor (equivalent to one batch). In order to overcome the overflow risk, the reactors were designed to 100% fill capacity include 20% for safety design; therefore, the height of reactor sizes are 1.5 times greater than the reactor diameter.

Detailed of the calculation regarding the design of reactors can be found in Appendix C. Table 5.2 shows the dimension specifications and materials of construction for each of the reactors. Since reactors (R101, R102, and R103) contain corrosive sulphuric acid, stainless steel (Carbon steel SA-285 grade C) was chosen as the material of construction. Carbon steel SA-285 grade C was also chosen for the transesterification reactor, because of the corrosive caustic being used as a catalyst. For the neutralization reactor, WD101, carbon steel was chosen as the material because the corrosive components will quickly be neutralized to prevent corrosion.

Vertical six blades were chosen as impellers to mix the mixture in the reactors. The diameter of the impeller, by convention, is 1/3 the tank diameter. The length of each blade is 1/8 the impeller diameter. To promote mixing within the reactor, two baffles (of width 1/12 times the tank diameter) were added to each reactor. The power requirement to drive the impeller is 0.5 Hp for the mixing of immiscible liquids for liquid-liquid reactions. As stated in Table 5.2 for the impeller specifications for each of the reactors.

The separator design calculation as referred to mass balance estimated the overall dimension of equipment shown in Table 5.2.

Table 5.2: Specification of equipment for biodiesel process using mechanical stirring

| No | Equipment | Specification |
|---|---|---|
| 1 | Mixer reactor 1 and 2 (R-101)<br>Function for preparation WCO and mix catalyst with MeOH | Capacity reactor = 0.13 $m^3$, diameter 510 mm, height 760 mm, thickness 3/16 in, material SA 515-70, max pressure 139 psi, type stirred reactor with vertical six blade include 2 baffle, the reactor equipped with oil heater until 120$^oC$, indicator level, pressure gauge and control temperature. Head and bottom reactor is a type ellipsoidal. |
| 2 | Esterification reactor (R-102)<br>Function for esterification process WCO | Capacity reactor = 0.13 $m^3$, diameter 510 mm, height 760 mm, thickness 3/16 in, material SA 515-70, max pressure 139 psi, type stirred reactor with vertical six blade include 2 baffle, The reactor equipped with oil heater until 120$^oC$, indicator level, pressure gauge and control temperature. Head and bottom reactor is a type ellipsoidal |
| 3 | Transesterification reactor (R-103)<br>Function for transesterification process WCO | Capacity reactor = 0.12 $m^3$, diameter 506 mm, height 760 mm, thickness 3/16 in, material SA 515-70, max pressure 139 psi, type stirred reactor with vertical six blade include 2 baffle, The reactor equipped with oil heater until 120$^oC$, indicator level, pressure gauge and control temperature.. Head and bottom reactor is a type ellipsoidal |
| 4 | Washing and distillation reactor (WD-101)<br>Function for washing FAME and evaporate water in FAME | - Capacity reactor = 0.15 $m^3$, diameter 535 mm, height 802 mm, thickness 3/16 in, material SA 515-70, max pressure 139 psi, type stirred reactor with vertical six blade include 2 baffle, The reactor equipped with oil heater until 120$^oC$, indicator level, pressure gauge and control temperature. Head and bottom reactor is a type ellipsoidal.<br>- Condenser type shell and tube, with shell side is water stream and tube side mixture stream, the diameter shell 3 in Sch no 40, length of shell 600 mm, diameter tube ¼ in, and amount of tube 18. |
| 5 | Separator tank 1 and 2 (S-101 and S-102)<br>Function for separation of ester from mixture MeOH-water | - Capacity reactor = 0.13 $m^3$, diameter 509 mm, height 764 mm, thickness 3/16 in, material SA 515-70. The reactor equipped with indicator level. Head and bottom reactor is a type ellipsoidal |

## 5.3 Summaries

Table 5.3 show the comparison of ultrasonic method with mechanical stirring. Both the methods have advantages and drawback process, but the author selected the mechanical stirring method for process biodiesel in 100 kg WCO/batch. The major point for consideration in comparison technique is cost of equipment which the system of mechanical stirring is cheaper than ultrasonic technique. The end of user for biodiesel process and product of biodiesel will be used to small industry in Batu Pahat.

Table 5.3: Comparison of existing technologies for biodiesel process (Chand, 2008; Colucci *et al*., 2005; Ji *et al*., 2006; Pinto *et al*., 2005)

| Variable | Ultrasonic | Mechanical stirring |
|---|---|---|
| Reaction Time | 5 - 60 minute | 0.5 - 3 hours |
| Reaction conditions | < 100 $^{o}$C | 0.1 MPa, 30-65 $^{o}$C |
| Catalyst | acid, alkali,metal oxide | acid or alkali |
| Free Fatty acids | methyl ester | saponified product |
| Yields | high | normal to high |
| Removal for purifications | methanol | methanol, catalyst, and saponified product |
| waste | waste water | waste water |
| glycerin purity | very high | low |
| process | simple | complicated |
| Cost (approximately) | RM 152300[a] (3 transducer ultrasonic, 3 reactor capacity 20 kg, and 2 separator) | RM 32000 (capacity 100 kg, 3 reactor, 2 separator and accessories) |
| Electricity consumption (kWh) | 1.04[b] | 0.18[b] |

[a)] Sebayang, 2011
[b)] Presentation in PECIPTA 2011, Sebayang *et al*., 2011

# CHAPTER 6

# CONCLUSION AND RECOMENDATIONS

## 6.1 Conclusion

This research has explored the application of ultrasonic tubular reactor to synthesis biodiesel from waste cooking oil in a close system reactor. In the optimal process it showed that molar ratio of WCO to MeOH of 1:6, NaOH catalyst of 1%wt, frequency ultrasonic of 20 kHz, ultrasonic output power of 650 Watt and 5 minute of reaction, produced ester contents of 96.54%wt. The novelty of this research is high ester contents yields with shorter reaction time, smaller amount of MeOH and NaOH catalyst.

The selection of method for pilot plant biodiesel process is mechanical stirring method. The pilot plant of biodiesel production was designed in 100 kg WCO/batch which this capacity followed the production of WCO in factory. Based on mass transfer, the design of equipment was calculated to determine the dimension reactor, separator and washing-distillation reactor.

## 6.2 Recommendations

(a) A scaled-up ultrasonic tubular reactor is further studies in designing the commercial production system with continuous system and also to determine energy require for transesterification through ultrasonic methods.

(b) The variety of feedstock for biodiesel process with high free fatty acid by ultrasonic tubular reactor need to be explored.

(c) The system of continues ultrasonic tubular reactor for next research must be explored to find the optimum condition of the biodiesel process (PRGS proposal 2011, Accepted).

(d) The heterogeneous solid catalyst in next studies will be explored to the ultrasonic system tubular reactor.

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